

THE CHARACTERISATION AND CETANE NUMBER DETERMINATION OF
SYNTHETIC DIESEL FUELS

BY

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for the degree of Master of Applied Science
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SUMMARY

South African synthetic fuel plants produce large quantities of lower alkenes which can be catalytically oligomerized to liquid transportation fuels. In the screening of experimental catalysts for the production of diesel-range fuels, it is important to measure the quality, as well as the quantity, of the fuel being produced. Cetane number is an important indicator of the quality of a diesel fuel and is measured by a standard engine test (ASTM D 613) which requires 1 litre of fuel and is therefore not suitable for the routine testing of the small volumes of fuel produced by experimental catalysts. Alternative cetane number prediction methods exist but these have generally been developed to predict the cetane number of crude-oil based fuels and are therefore not suitable for use with synthetically derived fuels.

This thesis details the development of a formula which accurately predicts the cetane number of a fuel from other, easily measured parameters.

Several samples of fuel were produced under varying reaction conditions and were hydrogenated to ensure that they were virtually 100% alkane. Differences in cetane number should therefore be due to differences in the degree of branching. By measuring the cetane number on a standard test engine and correlating the result with the amount of branching as measured by $^1\text{Hnmr}$, a formula was developed which was found to accurately predict the cetane number of these types of synthetic fuels.

The results obtained also show that for the conversion of ethene over a supported nickel catalyst, cetane number decreases as temperature increases. This decrease is probably caused by secondary butane oligomerization reactions.

CHAPTER 1

INTRODUCTION

Large quantities of light hydrocarbon gases are produced in the various cracking units found in oil refineries and by Sasol in their coal to liquid fuels process^{1,2}. These gases are generally too volatile for direct use in transportation fuels. To improve process yields, the alkenes present in the gas stream can be converted to liquid fuels using known conversion processes such as Universal Oil Products (UOP) catalytic condensation process which was first commercialised in 1935³. This process uses a solid phosphoric acid catalyst to oligomerize the C₃ and C₄ alkenes in the gas stream into petrol and diesel range transport fuels.

The main problem encountered with this catalyst is that the diesel product obtained is of a very poor quality. To overcome this problem new oligomerization catalysts are being developed to try and increase the quantity and quality of the liquid fuels produced. Current development is aimed at maximising the diesel fraction and improving its quality. The quality of a diesel fuel is a measure of its compliance with a number of standard tests which are detailed in a national diesel fuel specification⁴. Cetane number is often held to be the most important of these tests⁵ and is based on a comparison of the performance of the fuel under test to the performance of a standard reference fuel of known quality in a standard test engine^{6,7}. However, during catalyst development work the amount of fuel manufactured is usually insufficient for this type of test. Alternative testing

methods do exist but these were developed for fuels derived from crude oil and as such are not suitable for synthetic diesel fuels^{8, 9, 10, 11}.

It was anticipated that an alternative to the standard engine test could be found which would allow the quality of synthetic diesel fuels obtained by the oligomerization of the $C_2 - C_4$ alkenes to be determined. To achieve this it is necessary to understand the differences between the constituents of the synthetic diesels and those of crude-oil derived diesel and the effect these differences have on the quality of the fuel.

1.1 OLIGOMERIZATION

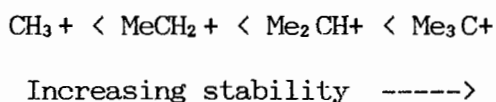
1.1.1 INTRODUCTION

The catalytic oligomerization of alkenes is the chemical process by which lower alkenes are converted into higher molecular weight products. The borderline between oligomerization and polymerisation is very vague with the only difference being that oligomerization products have a lower number of monomer units incorporated into the final product.

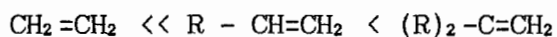
The types of synthetic fuels obtained by oligomerizing alkenes are to a great extent determined by the type of catalyst used and the severity of the conditions employed. Since this study is concerned with the quality of diesel range products it is useful to consider how different alkenes react over the main catalysts of interest i.e. acid catalysts and transition metal catalysts. Initial indications of the expected performance of the synthetic fuel produced can thus be gained.

1.1.2 ACID CATALYSIS

Heterogeneous acid catalysis is responsible for most of the processes (cracking and skeletal isomerisation of paraffins and alkenes, alkene oligomerization, alkylation of aromatic compounds, etc.) involved in the petrochemical and petroleum refining industry¹². It is generally accepted that these reactions proceed via a carbonium ion intermediate¹³ although it is possible that this is somewhat of an oversimplification¹². In the initiation process (see Figure 1.1) a hydrogen ion is added to the alkene in accordance with Markownikoff's rule leading to the formation of the most stable carbonium ion. Carbonium ion stability is as follows:-



In the carbon-carbon bond formation step of the oligomerization reaction, a carbonium ion adds to the alkene bond. Norton¹⁴ observed that the tendency for alkenes to react with carbonium ions is as follows:-



The dimeric carbonium ion may either lose a hydrogen ion to give the dimer or it may add to another alkene forming a trimeric carbonium ion. The degree of polymerisation is related to the ratio k_p/k_r of addition

(propagation) and proton loss (rupture). For the last reaction H^+ is either returned to the catalyst or transferred to an alkene molecule.

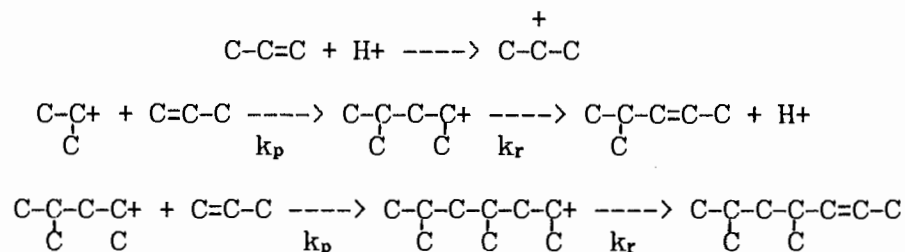


Figure 1.1: Acid catalysed oligomerization mechanism

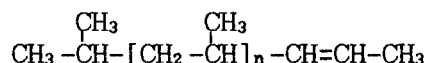
Internal alkenes react readily over acid catalysts whereas ethene remains virtually unconverted.

The commercial use of acid catalysts for the oligomerization of the lower alkenes is geared to the production of high octane petrol, with the result that diesel range products are of a low quality. For example, the diesel fuel obtained from the UOP catalytic condensation process which oligomerizes propene and/or butene to higher molecular weight compounds has been shown to have the properties listed in Table 1.1³.

Table 1.1: UOP Cat-poly product values

	As produced	Hydrotreated
Cetane No.	18	28
Bromine No.	108	1
ASTM		
Distillation °C		
10%	175	175
50%	182	182
90%	206	206

Even after hydrotreatment the product is still of a very low ignition quality and would have to be blended with a high ignition quality fuel feedstock in order to comply with the relevant specification. A low cetane number should be expected since, as has been discussed, the mechanism of this process involves carbonium ions and in the absence of steric constraints a highly branched product is inevitable. Analysis of the trimer and tetramer fractions of propene formed at 175-225°C and 30-70 bar show that isomers exhibiting the following branched structure are the main products¹³:-



This problem can be overcome by combining acid catalysis with shape selectivity. Certain acidic zeolites such as Mobil's H ZSM-5 show shape selective properties and it has been reported that the product obtained following oligomerization has the following properties¹⁵. (Table 1.2)

Table 1.2:
Oligomerization product of C₃+C₄ alkenes over ZSM-5

	As produced	Hydrotreated
Bromine number	79	4
Cetane number	33	56
90% boiling pt °C	333	343
Kinematic vis at 40°C	-	2.5

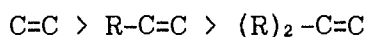
The hydrotreated oligomer has a high cetane number and can be blended with interior diesel stock. However, as with other acid catalysts low activity for the conversion of ethene is observed.

1.1.3 CO-ORDINATIVE TRANSITION METAL CATALYSIS

The commercial use of co-ordinative transition metal catalysis in the oligomerization of alkenes for the production of fuels is limited to homogeneous systems such as the Dimersol processes of IFP. In these systems, a Ziegler type nickel/aluminium alkyl catalyst is used for the production of high quality petrol. The catalyst has been modified so that dimerization is the predominant reaction.

The oligomerization mechanism in homogeneous systems has been well documented^{16, 17}. However, for heterogeneous systems there are still doubts as to the exact reaction mechanism.

Hogan *et al*¹⁸ used the carbonium ion theory to explain the production of hexenes in significant quantities during the dimerisation of propene on a nickel oxide catalyst supported on silica-alumina. At the same time the authors admitted that the reaction mechanism differed substantially from that found in the usual acid catalyst systems. Imai *et al*,¹⁹ using a similar catalyst system to Hogan, proposed the formation of cyclobutane derivatives as intermediate products. More recently Fel'dblyum *et al*²⁰ compared various homogeneous and heterogeneous transition metal catalyst systems and concluded that in both systems complex transition metal hydrides are responsible for the catalysis. The fact that ethene is readily oligomerized over these catalysts also suggests a different reaction mechanism. The reactivity of the alkenes over transition metal catalysts is the reverse of that seen over acid catalysts; namely:



Since carbonium ion intermediates are not involved in the reaction mechanism, a lower degree of branching should be evident in the final product obtained from transition metal catalysis.

On a laboratory scale it has been shown that nickel exchanged zeolite Y can oligomerize ethene into a petrol and diesel range product²¹. Although this system would not be suitable for a commercial operation due to rapid catalyst deactivation, other systems have been demonstrated which show no appreciable catalyst deactivation after operating continuously for 146 days. Initial diesel fuel quality studies indicated that a cetane number of at least 45 should be expected.

1.1.4 PRODUCT CHARACTERISATION

Increased insight into the nature of the liquid products obtained by the oligomerization of alkenes is desirable since this information can be used to determine the mechanism by which the oligomerization reaction is taking place. A number of methods have been used by various workers in this regard.

Chaffee *et al*²² used reaction gas chromatography/mass spectrometry to determine the molecular structure of individual C₇ alkenes present in a complex mixture of isomers formed by the co-oligomerization of C₃ and C₄ alkenes. Although a large number of compounds were identified, it was not possible to quantitatively identify all of the alkenes (C_nH_{2n})

present, as the number of isomers increases rapidly with n as can be seen from Table 1.3.

Table 1.3: Boiling points (°C) of the C₁ to C₈ alkanes and alkenes

1.	methane	-161,49
2.	ethene	103,71
3.	ethane	- 88,63
4.	propene	47,70
5.	propane	- 42,07
6.	2-Me-propane	- 11,73
7.	2-Me-propene	6,90
8.	1-butene	- 6,26
9.	n-butane	- 0,50
10.	tr-2-butene	0,88
11.	cis-2-butene	3,72
12.	2,2-di-Me-propane	9,50
13.	3-Me-1-butene	20,06
14.	2-Me-butane	27,85
15.	1-pentene	29,97
16.	2-me-1-butene	31,16
17.	n-pentane	36,07
18.	tr-2-pentene	36,35
19.	cis-2-pentene	36,94
20.	2-Me-2-butene	38,57
21.	3,3-di-Me-1-butene	41,24
22.	2,2-di-Me-butane	49,74
23.	4-Me-1-pentene	53,88
24.	3-Me-1-pentene	54,14
25.	2,3-di-Me-1-butene	55,67
26.	4-Me-cis-2-pentene	56,30
27.	2,3-di-Me-butane	57,99
28.	4-Me-tr-2-pentene	58,55
29.	2-Me-pentane	60,27
30.	2-Me-1-pentene	60,70
31.	3-Me-pentane	63,28
32.	1-hexene	63,48
33.	2-Et-1-butene	64,66
34.	cis-3-hexene	66,44
35.	tr-3-hexene	67,08
36.	2-Me-2-pentene	67,29
37.	3-Me-tr-2-pentene	67,63
38.	tr-2-hexene	67,87
39.	n-hexane	68,74
40.	cis-2-hexene	68,84
41.	3-Me-cis-2-pentene	70,45
42.	2,3-di-Me-2-butene	73,21
43- 87.	C ₇ alkanes and alkenes	72,49-98,50
88-197.	C ₈ alkanes and alkenes	99,24-125,66

Karlinsky *et al*²³ used gas chromatography to show that the principal components of a propene dimer formed over a silico-tungstic acid catalyst were 2-methyl-2-pentene, and 3-methyl-cis-2-pentene and 3-methyl-trans-2-pentene, suggesting that in the oligomerization of propene, true polymerisation and heteropolymerisation occur.

A number of workers used gas-liquid chromatography and ¹H NMR to analyse the products obtained during the oligomerisation of propene over a nickel oxide on silica-alumina catalyst^{19,20}. This information was used to highlight deficiencies in existing theories concerning this type of reaction.

Since total characterisation of the heavier C₇+ oligomerization product is often impossible, it often suffices to characterise the product by carbon number or to determine the hydrocarbon functional groups present. Galya *et al*²⁴ oligomerized propene over a number of zeolites and used high performance liquid chromatography (HPLC), ¹H NMR and ¹³C NMR to identify the hydrocarbon function groups (aromatic and alkene CH, alkene CH₂, methyl, methylene and methyne carbons) present in the liquid products. From these results they showed that the average molecular size and degree of branching of oligomers produced from zeolites is controlled mainly by the zeolite pore size.

From the above discussions it can be seen that to date, the laboratory scale oligomerization of alkenes into a diesel range produce has been concerned with the amount and not the quality of the diesel range product formed.

1.2 DIESEL FUEL QUALITY

1.2.1 THE DIESEL ENGINE

Great emphasis has been put on the quality of a diesel fuel. A better idea of the meaning of quality with respect to diesel can be obtained if one understands the working of a diesel, or as it is more correctly known, a compression ignition engine.

High speed diesel engines such as those used in trucks, buses, etc. work off a four stroke principle. On the first stroke air is compressed by the movement of the piston in the cylinder. Just before the end of the compression stroke, fuel is injected into the compressed air as a fine spray. The high temperature of the compressed air (at least 500°C)²⁵ causes spontaneous ignition of the fuel to occur which starts the power stroke of the engine. Ignition, however, is not instantaneous, there being a delay period between injection and ignition (See Figure 1.1). Fuel is injected continuously during this period resulting in the accumulation of unburnt fuel in the cylinder. When ignition occurs there is an initial rapid pressure rise as the accumulated fuel burns. If the delay period is too long, too much fuel will accumulate in the cylinder and the resulting explosive pressure increase can cause rough engine operation, misfiring and incomplete combustion, resulting in a loss of power and high smoke emission²⁶. The delay period can be broken down into two parts:-

i) a physical delay, which is the time required for the injected fuel to evaporate and mix with enough air to be flammable.

ii) a chemical delay, which is the time required for precursors to form in the flammable mixture.

The physical delay constitutes about 5-10% of the total delay. The total delay is therefore a function of both the engine design and the chemical composition of the fuel. Collectively these physical and chemical properties which affect the delay period are known as the ignition quality which is expressed as the cetane number.

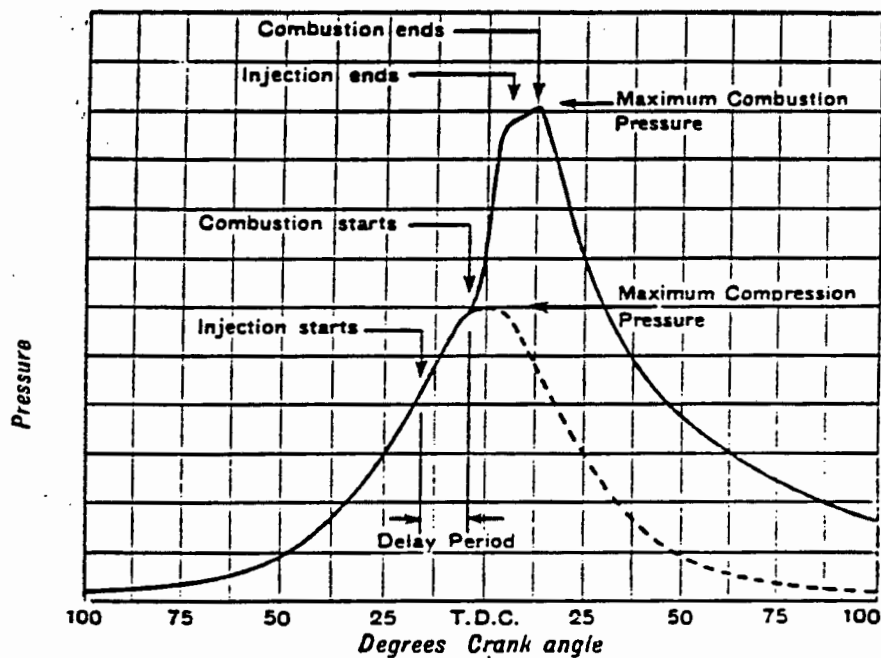
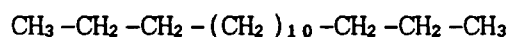


Figure 1.2: Rate of pressure rise versus degrees crank angle

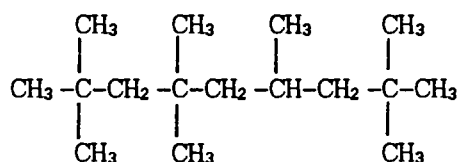
1.2.2. CETANE NUMBER

The cetane number scale for diesel fuel is similar to the octane number scale for petrol in that it is an arbitrary scale measured from 0 to 100 and used high and low ignition quality standards. Hexadecane (cetane)

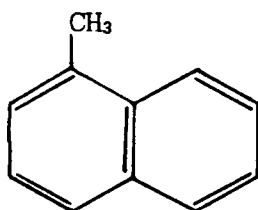
is used as the high ignition quality standard and represents 100 on the scale and 2,2,4,4,6,8,8-heptamethylnonane (HMN) is used as the low ignition quality standard and represents 15. Zero is represented by α -methyl naphthalene, a coal tar product (Figure 1.3).



Cetane $\text{C}_{16}\text{H}_{34}$



2,2,4,4,6,8,8-Heptamethylnonane $\text{C}_{16}\text{H}_{34}$



α -Methylnaphthalene $\text{C}_{11}\text{H}_{10}$

Figure 1.3: Primary standards

Both cetane and HMN are expensive so secondary reference fuels are used in routine testing. These are supplied by Phillips petroleum. The high reference fuel has been designated T18 and has a cetane number of 75 and the low reference fuel has been designated U11 and has a cetane number of 20.5.

1.2.3 THE ENGINE TEST

The cetane number measurement is made in a single cylinder, variable compression engine and is defined as the % cetane + 0.15 (% HMN) of a blend of cetane and HMN which has the same ignition quality as the fuel being tested. The test method is fully described in ASTM D613 or IP 41. Briefly, the fuel being tested is run in the engine and the compression ratio is changed until the delay period is equivalent to a crank angle of 13 degrees. When the compression ratio giving the standard delay has been found, no other adjustments are made to the engine. Reference fuels are then used until a blend is found which matches the fuel being tested. The cetane content of this reference fuel blend is taken as the cetane number of the fuel under test.

It should be recognised that the cetane number of a fuel is therefore a measure of the fuels ignition characteristics under one set of conditions (Table 1.4) and is not necessarily representative of a fuels ignition characteristics under other operating conditions. This might explain why some fuels of low cetane number perform well in practice. Despite these limitations, the cetane number certainly serves a purpose and its usefulness as an indication of a fuels ignition quality cannot be denied.

Table 1.4: Operating conditions for the standard engine test

Inlet temperature 66°C
 Jacket temperature100°C
 Speed900 rpm
 Injection timing 13 degrees btdc

rpm = revolutions per minute
 btdc = before top dead centre

The precision of ASTM D613 is shown in Table 1.5.

Table 1.5: Repeatability and reproducibility limits of ASTM D 613

Average Cetane Number	Repeatability Limits	Reproducibility Limits
40	0,6	2,5
44	0,7	2,6
48	0,7	2,9
52	0,8	3,1
56	0,9	3,3

The repeatability limits refer to the maximum allowable difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on the same material. Similarly, the reproducibility limits refer to the difference between two single and independent results obtained by different operators working in different laboratories on identical test material.

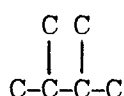
1.2.4 CHEMICAL STRUCTURE AND CETANE NUMBER

The pioneering work of Ricardo²⁶ in England and Boerlage and Broeze²⁷ in Holland showed that the high speed diesel engine was quite sensitive to fuel ignition quality. To understand the differences in ignition quality of diesel fuels, one must look at the chemical composition of the fuel. A diesel fuel is a complex mixture of a great many different hydrocarbons which can be classified into a smaller number of hydrocarbon groups (alkanes, cycloalkanes, aromatics, etc). It has long been known that the relative abundance of one or another of these groups has a marked effect on the ignition quality of the fuel. In 1935 Boerlage and Broeze proposed that ignition quality decreased in the order alkanes, alkenes, monoaromatics and condensed aromatics²⁸. Backhouse and Ham separated diesel fuels into aromatic and saturate fractions and showed that cetane number decreased with increasing aromatic content.²⁹ However, not all aromatics are detrimental to the ignition quality of a fuel. Wood and Garner showed that the cetane number of the alkyl benzenes increased with increasing alkyl chain length^{30, 31}. Thus as the alkane chain attached to the benzene ring increases in length so too does its effect on the chemistry of the molecule.

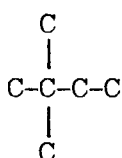
Hinshelwood studied the effect of chemical structure on the rate of oxidation of hydrocarbons³² and showed that for the n-alkanes the rate of oxidation increased exponentially with an increase in chain length. The values relative to pentane are as follows:

Propane	Butane	Pentane	Hexane	Octane	Decane
0.1	0.5	1	7.5	200	1380

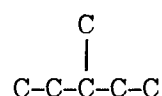
The influence of branching was equally remarkable as can be seen from the following figures which show the relative oxidation rates of isomers of hexane:



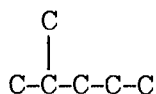
1



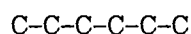
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60

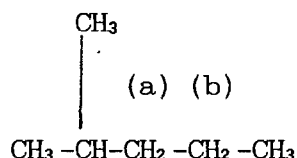


560



1580

Hinshelwood explained these results by proposing that the presence of a methyl group negatively influenced the rate of oxidation and that intervening CH_2 groups reduced this effect. Hinshelwood ascribed to the methyl group an "antagonising influence" which was either 1, $1/3$ or $1/9$ depending on whether the carbon atom in question was adjacent, one removed or two removed from a methyl group. In addition, the influences of all the methyl groups are additive. For example in:



the influence at (a) is $1/3 + 1/3 + 1/3 = 1$

while that at (b) is $1 + 1/9 + 1/9 = 1.22$

Thus for any given hydrocarbon, Hinshelwood could calculate at which carbon atom the methyl group effect was least and showed that oxidation occurred at a rate which was some function of this factor.

Livingstone³³ expanded this theory that resistance to oxidation was a function of structural factors. He put forward a number of rules for the calculation of "structural retardation factors" of hydrocarbons. He not only studied the retarding effects of the methyl group but also other groups such as vinyls, naphthenes, tertiary alkyls etc. The greatest retarding effects were attributed to aromatic CH groups followed by tertiary alkyl groups and methyl groups, the latter two groups being typically associated with isomers of the n-alkanes. From this work a correlation between structural retardation factor and octane number was developed.

$$\text{ON} = \frac{0.58 * (\text{SRF}) - 2.12}{100} \quad (1.1)$$

$$3.5 - 0.057 * (\text{SRF})$$

where ON = Octane number

and SRF = Structural retardation factor

Octane number can be thought of as the antithesis of cetane number. A fuel exhibiting high quality combustion properties in a spark-ignition engine would be associated with poor performance in a diesel engine. In fact, one of the original suggestions for expressing diesel fuel quality was to use a heptane value³⁴, heptane being the low ignition quality fuel used in the octane rating of petrols.

From Hinshelwood and Livingstone's results it can again be seen that for a diesel fuel to have a low delay period between injection and ignition (high cetane number) the fuel should contain a high proportion of linear compounds.

The effect that structure has on ignition quality can be measured directly through the engine testing of pure hydrocarbons. Workers such as Olson et al³⁵, Pucket and Caudle³⁶, and Wood and Garner^{30, 31} have contributed in this regard. These workers confirmed the general ignition quality trends of the hydrocarbon groups, namely that the ease of ignition decreases in the order n-alkanes, naphthenes, branched alkanes and aromatics. Figure 1.3 shows this trend graphically. However, considering the great number of compounds in the diesel boiling range relatively few cetane number engine tests of pure compounds have been carried out. In particular, the data reveals the lack of a systematic approach especially with regard to the branching of the alkanes. For example, it has not been clearly established how the ignition quality changes as a function of the position of a methyl group in an alkyl chain. One reason for the lack of data in this regard is the cost of testing, (i.e. the availability of pure compounds in sufficient quantity).

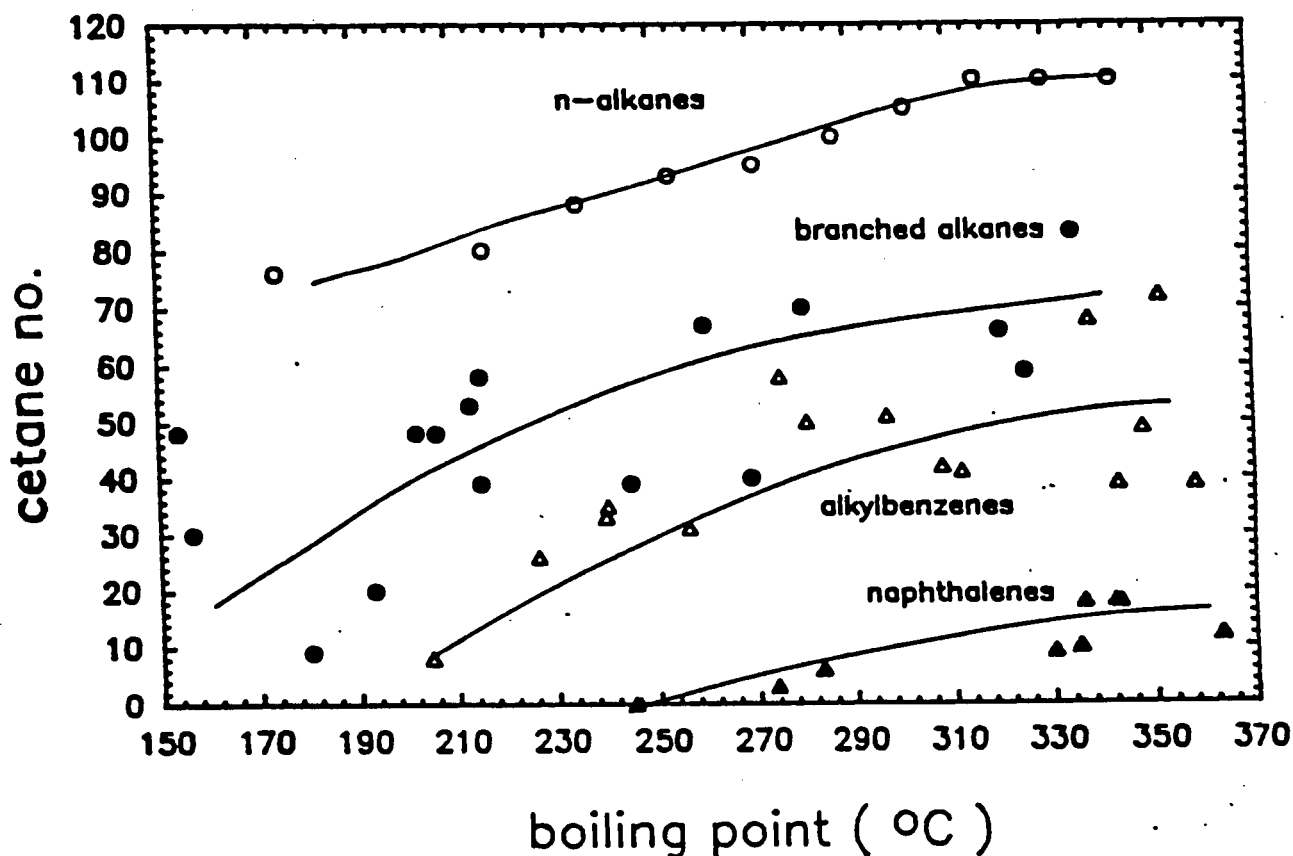


Figure 1.4: Cetane number as a function of boiling point

1.2.5 ALTERNATIVE METHODS FOR CETANE NUMBER DETERMINATION

1.2.5.1 Correlation Studies

Since the inception of the engine test as the main criterion for determining diesel fuel quality, attempts have been made to correlate cetane number with other more easily measured physical properties such as density, volatility, aniline point etc. In general these correlations reflect the chemical composition of the diesel fuel.

A brief history of the evolution of cetane indices and the reason behind the inclusion of the various terms forming the indices follows. The first generally accepted correlation appeared in 1934 and was termed the "Diesel Index"³⁷. The diesel index of a fuel is defined as follows:-

$$\text{Diesel Index} = \frac{\text{Aniline Point (}^{\circ}\text{F)} * \text{API Gravity}}{100} \quad (1.2)$$

The aniline point is the lowest temperature at which equal parts by volume of the fuel and freshly distilled aniline are completely miscible and is inversely dependent on the amount of aromatics and unsaturated hydrocarbons present in the sample. Thus a high aniline point indicates a high alkane content and a low aniline point a high aromatic content.

The API Gravity is defined as:-

$$\text{API} = \frac{141.5}{\text{SG}} - 131.5 \quad (1.3)$$

where SG = specific gravity

and API = American Petroleum Institute

and is inversely proportional to the density of the fuel. Since aromatic compounds have a higher density than alkanes, a high fuel density indicates a high aromatics content. Therefore, to obtain a high diesel index, a low fuel density (low aromatic content) and high aniline point (high alkane content) are required.

As an ignition quality predictor this formula has its limitations but is nevertheless widely used around the world and is quoted as a standard IP test method³⁸.

In 1937, a method based on the analysis of a diesel fuel in terms of the content of aromatics, naphthenics, and paraffinic side chains was proposed³⁹:-

$$\text{Cetene value} = -0.2A + 0.1N + 0.85P \quad (1.4)$$

where A = aromatics content

N = naphthenics content

and P = paraffinic side chain content

Originally, cetene was used as the high ignition quality standard but owing to variations in the quality of different batches of cetene, cetane was adopted as the high quality reference fuel.

Once again emphasis is placed on the "paraffin" content of the diesel fuel. Although this method is more accurate than the diesel index it did not find favour owing to the complicated analytical techniques required for its application.

By 1944, a large number of different correlation formulae were being used. In an attempt to standardise correlation procedures the diesel index panel of standardisation sub-committee No. 4 was set up to assess the main formulae being used and to determine which was the most reliable⁴⁰. They reached the conclusion that the most reliable formula was:-

$$\text{Calculated Cetane Number} = 175.4 * \log(\text{MBPt}^\circ\text{F}) + 1.98 * (\text{API Gravity}) - 496 \quad (1.5)$$

where MBPt = Mid-boiling point

For the sake of brevity, it was also decided that the cetane number so calculated would be called the cetane index.

The mid-boiling point of a sample is the temperature at which 50% of the sample is recovered when it is distilled in accordance with standard test methods IP 123 or ASTM D86. Figure 1.4 showed that for pure hydrocarbons, the cetane number increases with boiling point. If a diesel fuel is distilled and separated into small fractions a similar relationship is seen (Figure 1.5). Therefore, the higher the mid-boiling point the higher the calculated cetane number.

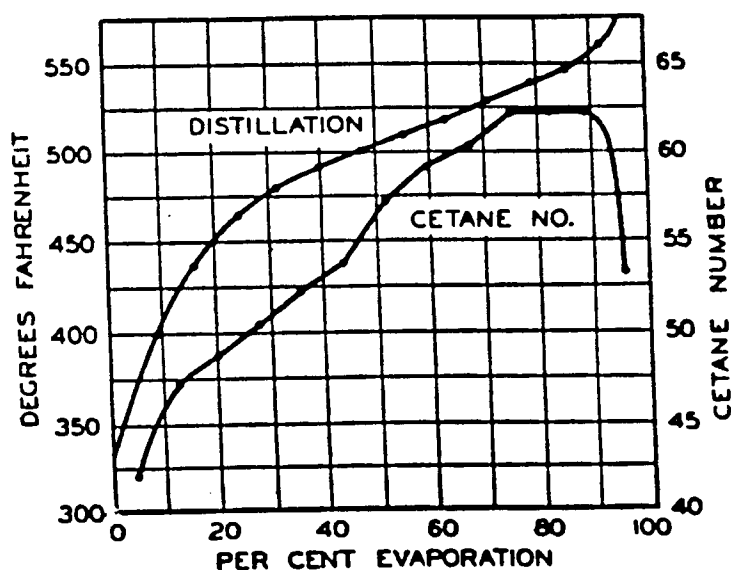


Figure 1.5 : Cetane numbers of diesel fuel fractions

This formula has since been modified a number of times which is indicative of changes in the composition of diesel fuels caused by changes in the types of crude-oil refinery operations used. The versions of this formula which are in use today constitute the main cetane number prediction formulae^{6, 7}.

When the diesel index and cetane index formulae were compared it was concluded that the cetane index was the more reliable method by which to estimate the cetane number of a diesel fuel.⁴¹ Figure 1.6 shows plots obtained during the comparison programme.

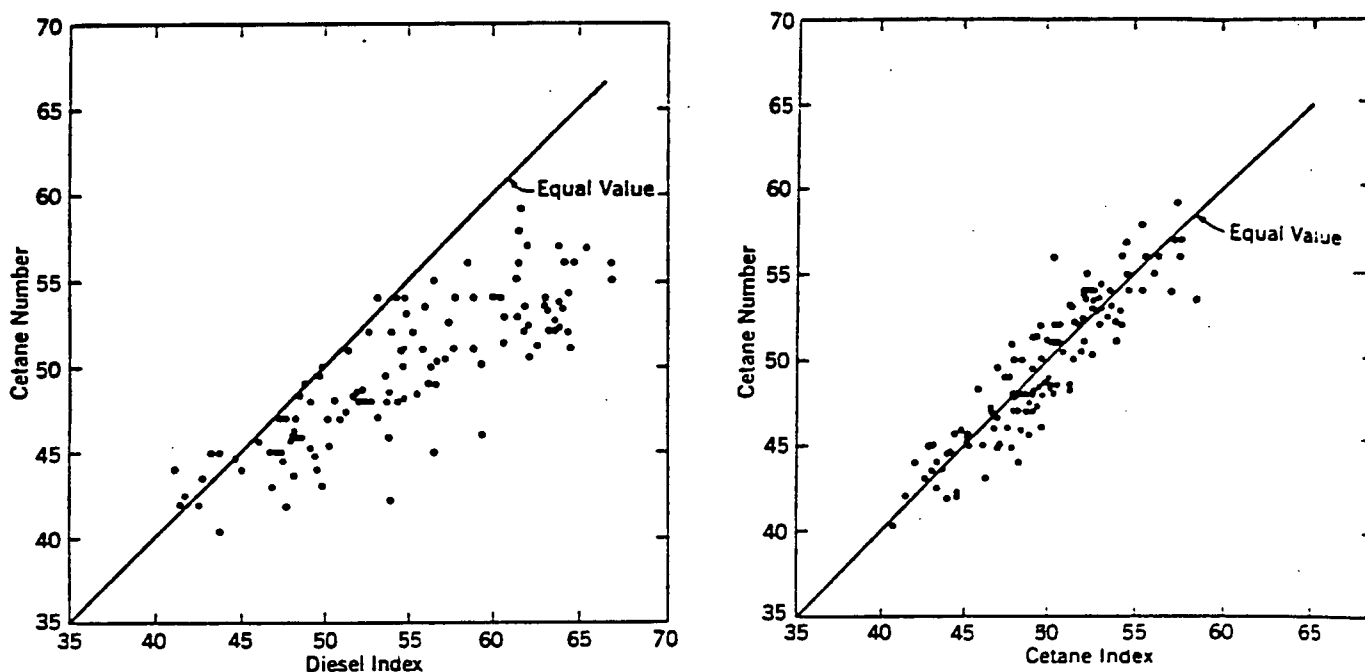


Figure 1.6: Comparisons of diesel index and cetane index with cetane number

As can be seen from figure 1.6, the diesel index tends to overrate the test samples. However, it is also clear that a relationship does exist between diesel index and cetane number and that with a modification of the diesel index formula, a better correlation could be obtained.

The use of aniline point is currently out of favour because it is not a routine quality control test. There is also a reluctance to use aniline due to its toxicity. Aniline point is, however, a powerful predictor. A study by Unzelman and Collins⁴² of the data used in formulating the most recent cetane index equation yielded the following

formulating the most recent cetane index equation yielded the following five-term aniline point equation:-

$$\begin{aligned} \text{CN} = & 16.419 - 1.1332(\text{AP}/100) + 12.9676(\text{AP}/100)^2 \\ & - 0.2050(\text{AP}/100)^3 + 1.1723(\text{AP}/100)^4 \end{aligned} \quad (1.6)$$

where AP = aniline point

It was concluded that this equation was a definite improvement over the official ASTM D976-80 equation.

Another physical property which is sometimes used in prediction methods is kinematic viscosity. If the viscosity of a fuel is too low, the more frequent maintenance of the injection system may be necessary, whereas too high a viscosity can result in excessively high pressures in the injection system. It is possible that future diesel engines will make greater use of electronic control systems which can optimise engine operation by continuously monitoring various properties of the fuel. Using this data, the injection system could then be regulated, thereby increasing or decreasing the amount of fuel injected as necessary. A limitation is that it must be possible for the property to be measured electronically. Density and viscosity are the only commonly measured properties discussed so far which fulfil this requirement. With this in mind Henein *et al* obtained a correlation of the form⁴³:-

$$\text{CN} = 32.98 + 38.74 * \frac{\text{Log KV}}{\text{SG}} \quad (1.7)$$

SG

where KV = kinematic viscosity

and SG = specific gravity

This correlation is very specific since the data base consisted of a number of "alternative" fuels such as indolene and their blends and therefore cannot be expected to give a good correlation for "normal" diesel fuels.

As has been previously mentioned, the physical properties used in correlations are influenced by the carbon groups present in the fuel and therefore infer rather than specify what the molecular structure of a fuel is. The National Research Council of Canada (NRCC) developed a cetane index based on combinations of physical properties which were specifically chosen to relate as closely as possible to the chemical structure of the diesel fuel under test. However, although the NRCC index was found to be an improvement over existing indices, the test procedure is lengthy and involves the determination of a fuels density, distillation, viscosity and aniline point.

Since the ignition quality of a fuel depends more on its chemical composition than on any other factor, it would be better to base cetane number prediction methods on compositional analysis than on physical properties. For compositional analysis a method is required which can identify and quantify the various hydrocarbon types present in the fuel. The test methods discussed so far do not give this type of information and therefore other methods must be used. ^1H and ^{13}C nuclear magnetic resonance (NMR) are used routinely in the compositional analysis of hydrocarbons and can provide the basis of a potential test method for diesel fuels.

1.3 NMR IN CORRELATION STUDIES

An analytical method which can be applied to complex hydrocarbon mixtures is nuclear magnetic resonance spectroscopy (NMR). There are many standard texts explaining the theory and workings of NMR^{44, 45} in great detail. However, a somewhat simplified explanation for the origin of NMR follows. NMR works on the principal that certain nuclei possess an intrinsic magnetic moment which results from the spin angular momentum of the nuclei. Transitions between the energetically poorer to the energetically richer spin states give rise to the NMR phenomena.

The intrinsic nuclear magnetic momenta are quantised and can be expressed as Ih where h is the Planck constant divided by 2π and I is the spin quantum number. Each individual nucleon (neutron or proton) has a spin quantum number of $1/2$. If the atomic mass is odd then the quantum number is a half-integer [^1H ($1/2$), ^{15}N ($1/2$), ^{23}Na ($3/2$)]. It is an integer if the atomic mass is even and the atomic number is odd [^2H (1), ^{14}N (1)], and it is zero if both the atomic mass and atomic number are even [^{12}C , ^{16}O]. The nuclei of the isotopes which have a spin quantum number of $I=0$ are non-magnetic.

Nuclei with a non-zero spin angular momentum can be represented as rotating electrical charges and hence as magnetic dipole moments. In the presence of a static magnetic field the magnetic moment precesses around the magnetic field (see Figure 1.7). This is known as the Larmor precession.

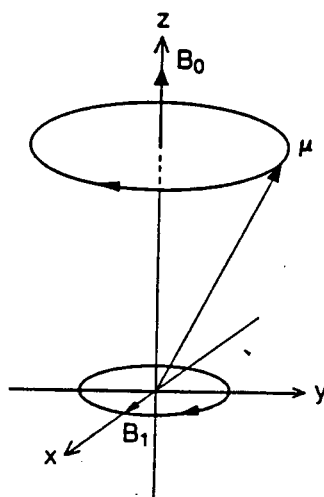


Figure 1.7: Precession of a magnetic moment μ in a magnetic field B_0

In addition to the static magnetic field B_0 , a small oscillating magnetic field B_1 with the same frequency and direction as the Larmor precession is applied perpendicular to B_0 . The magnetic moment μ thus experiences a torque away from B_0 . In a collection of nuclei all precessing about B_0 there will be two energy states corresponding to the dipoles either being parallel to or oriented against the direction of the external magnetic field. These two states will be at two different energy levels and hence there is a population difference between them which results in a net magnetisation along B_0 . Since μ is very small, the energy involved in a transition of a single spin from one energy level to another is also very small. Thus a large number of nuclei are necessary to observe these transitions which are caused by field B_1 . When the frequency of B_1 matches the Larmor precession frequency, transitions occur between the energy levels. NMR spectroscopy detects the net energy changes resulting from these transitions.

This is achieved in practice by using a radio-frequency (RF) as the source of the oscillating magnetic field and a magnet to provide a stable and homogeneous static field.

The above explanation would suggest that all nuclei of the same isotope in the same magnetic field would have the same resonance frequency. However, the nuclei in atoms are surrounded by electrons which also interact with the magnetic field. The electrons shield the nucleus from the applied magnetic field. However, in molecules there is more than one charged nucleus which can hinder the circulation of the electron cloud about any specific nucleus. This combination of magnetic fields is thus a consequence of the molecular environment of the nucleus and gives rise to the phenomenon known as the chemical shift. The chemical shift is proportional to the strength of the applied field and therefore differs between NMR spectrometers making the direct comparison of results difficult. This is overcome by reporting chemical shifts relative to that of a reference substance such as tetramethylsilane (TMS). The scale used is the δ scale with δ being defined as:

$$\delta = \frac{\nu_{\text{obs}} - \nu_{\text{standard}}}{\nu_{\text{standard}}}$$

where ν = the resonance frequency

The two types of atom of immediate relevance to the application of NMR to hydrocarbon analysis are ^1H and ^{13}C . By use of NMR it is possible to differentiate between the various types of carbon atoms present and to

acquire information regarding their short range environment. Figure 1.8 shows the high and low reference fuels used in cetane number determinations with the different carbon types identified.

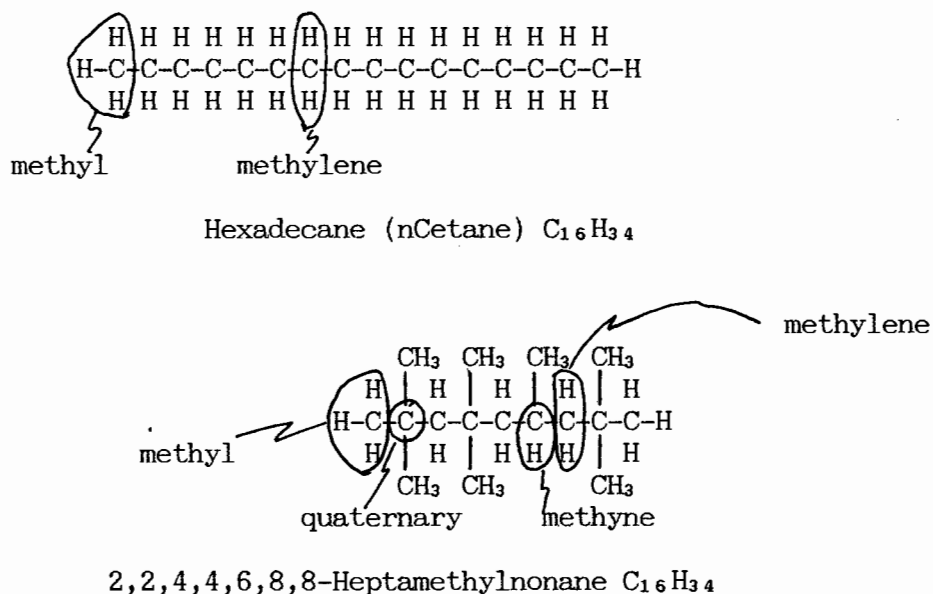


Figure 1.8: Different carbon types present in high and low reference fuels

As a result of the chemical shift, an NMR spectrum shows several peaks which are indicative of the different types of carbon atoms. An advantage of NMR is that no calibration is necessary for the evaluation of the intensities of the peaks and the area under an NMR peak is directly proportional to, for example, the number of hydrogen atoms giving rise to the peak.

Thus for n-cetane, two peaks (due to CH_2 and CH_3 groups) will be observed, showing a peak ratio of CH_2 to CH_3 hydrogens of 28:6. NMR can also be used to analyse hydrocarbon mixtures where information regarding hydrocarbon functional groups can be obtained⁴⁶. It has also been used

extensively in the characterisation of fossil fuels and products derived from such fuels. ^1H NMR is most often used for the qualitative analysis of pure hydrocarbons, structural analysis, and in the determination of functional groups. Functional group analysis is based on the premise that although a hydrocarbon mixture may be rather complex, containing many compounds, the number of different functional groups present is relatively low⁴⁷. The advantage of this method when used to determine the quality of a diesel fuel is that the cetane number is obtained from relevant structural parameters on a molecular level rather than more arbitrary physical properties of the bulk material.

1.3.1 ^1H NMR CORRELATION STUDIES

Despite the fact that it is possible to use NMR to predict a wide range of diesel fuel properties, its use in fuel ignition quality studies has been somewhat limited. Cookson *et al*^{48, 49} have used both ^1H and ^{13}C NMR in conjunction with HPLC to study diesel and kerosene fuels obtained from crude oil and synthetic fuel sources. Simple linear relationships between fuel composition and a range of fuel properties were derived with good correlations being obtained for most properties.

One of the first uses of ^1H NMR in a cetane number correlation study related cetane number to the structural composition (by carbon atom type) of a diesel fuel⁵⁰. The spectra of the samples were divided into four regions and the signals assigned to various carbon types. Namely:-

Ca = carbon atoms present in aromatic rings

C α = carbon atoms α to aromatic rings

C2 = alkane CH₂ and CH; CH₂ and CH₃ β to aromatic rings; CH₂ γ to aromatic ring.

C3 = Alkane CH₃; CH₃ γ to aromatic ring

134 diesel fuels of known cetane number were analysed and the following correlation developed⁵¹:-

$$\text{GCN} = 111.2387 - 28.2098/\text{Ca} - 0.1048\text{Ca}^{1.5} + 1.1533\text{C}\alpha - 7.8111\ln\text{C}\alpha + 0.0853\text{C2} - 1.5036\text{C3} \quad (1.9)$$

where GCN = calculated cetane number

This correlation was further improved by confining the selection of data obtained to only 67 of the original 134 samples. This was done because the cetane numbers for these 67 fuels had been determined from more than one test engine so a higher degree of reliability could be attached to the results. The improved correlation is of a similar form:-

$$\text{GCN} = 24.3848 - 286.728/\text{Ca} + 587.3567/\text{Ca}^2 + 1.5227\text{C}\alpha - 15.8821\ln\text{C}\alpha + 0.9778\text{C2} + 0.0047\text{C2}^2 - 0.2835\text{C3} + 0.002\text{C3}^2 \quad (1.10)$$

As with the original correlation studies based on the physical properties of the sample, the above correlations base their predicting powers on whether the carbon types are aromatic or not. It can be seen that as the aromatics content tends towards zero the GCN will tend towards infinity. This type of correlation will therefore generally

not be suitable for predicting the ignition quality of aromatic-free diesel fuels such as those obtained by alkene oligomerization.

This problem was addressed in a study which correlated cetane number with the relative hydrogen population of the sample⁵². Two formulae were presented. One predicted cetane number for saturated fuels and the other predicted cetane number for fuels containing aromatic components.

a) For non aromatic hydrocarbon fuels

$$\text{Cetane number} = -54 + 1.018 * (dH)CH + 0.1595 * (dH)CH_2 \quad (1.11)$$

where d = density

H = wt % hydrogen content

CH = % methylene hydrogen of total hydrogen

CH₂ = % methylene hydrogen of total hydrogen content

b) For aromatic hydrocarbon fuels

$$\begin{aligned} \text{Cetane number} = & 9.49 - 0.0298 * (dH)CH_3 + 0.0896 * (dH)CH_2 \\ & + 0.000097 * (dH)S^2 - 0.038 * (dH)ALP \end{aligned} \quad (1.12)$$

where d = density

H = wt % hydrogen content

CH₃ = % methyl hydrogen of total hydrogen content

CH₂ = % methylene hydrogen of total hydrogen content

S² = sum of % alkyl hydrogen

ALP = % alpha hydrogen (hydrogens adjacent to an aromatic ring)

A trial index based on compositional analysis⁵³ used high performance liquid chromatography (HPLC) to determine the percent total saturates, monocyclic and dicyclic aromatics and ¹H NMR to subdivide the saturates into percent straight and branched chain saturates. This fractionation was based on the CH₂ to CH₃ ratio since these proton types are representative of straight and branched chain saturates respectively. The equation obtained was of the form:-

$$\begin{aligned} \text{CI} = & 49,321 + 0,568 (\% \text{ straight chain saturates}) - 0,600 (\% \\ & \text{branched chain saturates}) - 0,317 (\% \text{ monocyclic aromatics}) \\ & - 0,582 (\% \text{ dicyclic aromatics}) \end{aligned} \quad (1.13)$$

where CI = cetane index

From this equation it can be seen that for diesel fuels consisting purely of alkanes (such as those expected after hydrogenating alkene oligomerization products) the aromatic terms will fall away and it should be possible to determine the cetane number without using HPLC.

On the fuels analysed, this index proved to be a better predictor of cetane number than ASTM D4737-87, ASTM D976-80 and the index determined by Bailey *et al.*

One of the problems with ¹H NMR is that the peak intensity attributed to CH₂ groups which are representative of straight chains and therefore have a strong positive effect on cetane number can be overlapped by species which do not have the same strong effect (e.g. methyl groups

beta to an aromatic). This would cause the cetane number to be overestimated.

1.3.2. ^{13}C CORRELATION STUDIES

The above problems can be overcome to some extent by using ^{13}C NMR. ^{13}C NMR is a useful technique for the analysis of hydrocarbons because it provides direct information on the structure of the carbon skeleton. Cetane number correlation studies which have used ^{13}C NMR are, like those based on ^1H NMR, limited. Those that are available use similar principles to those employed in ^1H NMR. For example Danaher and Johnstone⁵⁴ developed correlations relating cetane number to hydrogen content and aromaticity. The relationships obtained were:-

$$\text{Cetane number} = 21.4 + 9.79 \times 10^{-6} * [\text{H wt\%}]^{5.75} \quad (1.14)$$

and

$$\begin{aligned} \text{Cetane number} = 54.1 - 0.257 [\text{1 ring aromatics}] - \\ 0.377 [\text{2 ring aromatics}] \end{aligned} \quad (1.15)$$

Indritz *et al* used a different approach, namely group additivity⁵⁵. With this method it is assumed that a hydrocarbon is made up of a certain number of functional groups. For example, if one examines the simplest of the hydrocarbon series, the alkanes, one can see that as one progresses through the series, changes in properties can be attributed to the addition of methylene groups. It should therefore be possible to assign hypothetical cetane numbers to each functional group. Table 1.5

lists the groups used by Indritz *et al* in their correlation as well as their estimates of cetane number.

Table 1.6: Carbon Groups and their associated cetane numbers

<u>Cetane number</u>	<u>Group</u>	<u>Definition</u>
10	Methyl	CH ₃
22	α methylene	CH ₂ α to one or two CH ₃ , CH or C
87	β methylene	CH ₂ β to one or two CH ₃ , CH or C
135	γ methylene	CH ₂ γ to one or two CH ₃ , CH or C
84	Methyne	CH
-20	Quaternary	C
0	Phenyl	C or CH

The authors claimed that the choice of the integration regions was not critical provided that the group additivity principle was applied to the spectra using any reasonable integration regions.

In a study by Gautier⁵⁶ correlation methods using both ¹H and ¹³C NMR were developed.

For ¹H NMR, the expression obtained was of the form:-

$$CCI = -0,0571H_3 + 0,935H_2 - 0,454H_1 - 9,718H_A + 0,102H_D \quad (1.16)$$

where CCI = Calculated cetane index

H₃ = All methyl hydrogens with the exception of those

attached directly to an aromatic.

H_2 = All methylene and methyne hydrogens with the exception of those attached directly to an aromatic.

H_1 = All hydrogens on carbon groups attached directly to an aromatic.

H_A = All mono-aromatic hydrogens.

H_D = All poly-aromatic hydrogens

This equation would reduce to:

$$CCI = -0,0571H_3 + 0,935H_2 \quad (1.17)$$

for fuels containing no aromatics.

The regression equation calculated for the ^{13}C NMR was:-

$$\begin{aligned} CCI = & -0,0125C_{aro} + 0,439CH_3 - 0,175 CH_{31} - 0,279CH_{21} + \\ & 0,831CH_2 + 1,396CH_{23} + 0,662CH_{22} + 0,294CH + \\ & 0,889CH_{2aro} + 0,502Naph \end{aligned} \quad (1.18)$$

where C_{aro} = Aromatic carbons.

CH_3 = Methyl groups at the end of a long chain

CH_{31} = Methyl groups attached to an aromatic or a carbon chain

CH_{21} = Methylene groups α to a methyl group at the end of a long chain.

CH_{22} = Methylene groups β to a methyl group at the end of a long chain.

CH_{23} = Methylene groups γ to a methyl group at the end of a long chain.

CH = Methynes

CH₂_{aro} = Methylene groups attached to an aromatic.

Naph = Naphthenic carbons.

CH₂ = Methylene groups not described above.

It was concluded that the two methods were equivalent, but overall there were more points in favour of ¹H NMR especially with regard to speed of data acquisition.

1.4 CONCLUSION

The cetane number of diesel fuels derived from crude oil and to a lesser extent those derived from coal processes, has been correlated with various physical and molecular parameters. However, what is still required is a method by which the cetane numbers of the mainly alkane synthetic diesel fuels derived from oligomerization processes can be estimated. Cetane number correlation methods involving physical test methods do not predict well for synthetic fuels and still tend to require too much sample. Of the methods involving NMR, ¹H NMR appears to be the most suitable method for this work.

1.5 AIMS OF THIS STUDY

The aim of this study is to develop a correlation method capable of predicting the cetane number of diesel fuels obtained by the oligomerization of the lower alkenes. The method developed should enable a close prediction of engine test cetane numbers to be made. However, in a research situation where the primary objective is the

evaluation of catalyst performance, an estimate of cetane number (± 5 cetane numbers for example) is often all that is required, at least in initial catalyst testing studies. A much tighter correlation would be required by a refinery where overestimating or underestimating by the above margin could not be tolerated, largely on economic grounds.

CHAPTER TWO

EXPERIMENTAL

2.1 REACTOR SYSTEMS

Oligomerization product was obtained from a number of reactor systems, details of which are given below.

2.1.1 MICRO-REACTOR SYSTEM

A micro-reactor system was used for screening potential oligomerization catalysts and is shown schematically in Figure 2.1. Ethene feed was stored in a high pressure cylinder while propene and butene were stored in liquid petroleum gas (LPG) cylinders.

When feeding ethene, the gas flowed from the cylinder, over two purifying columns containing zeolite 5A and a BASF R3-11 catalyst respectively. The ethene then passed through two solenoid valves via a 60 μ m frit filter. Flow control was maintained by a Brooks mass flow controller which was set and read from a control panel mounted on the front of the reactor system. The gas was then led via a non return valve to an inlet manifold which was connected to the reactor. System pressure was set using a back pressure regulator across which the pressure dropped to one atmosphere. After the back pressure regulator, the product could either be directed to a gas chromatograph for on-line analysis or to a condenser where the liquid phase condensed. The gas phase was monitored using a wet gas meter before being vented to the atmosphere.

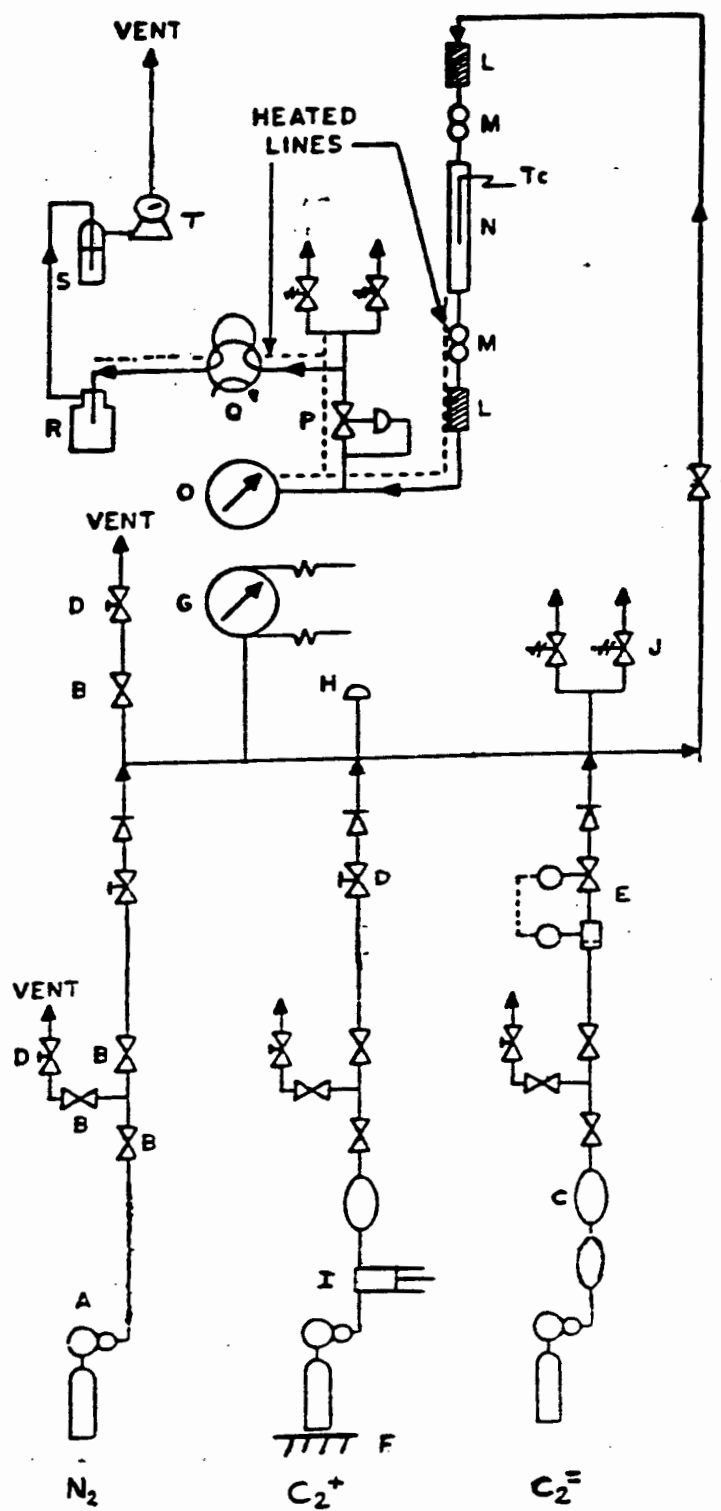


Figure 2.1 Micro-reactor system

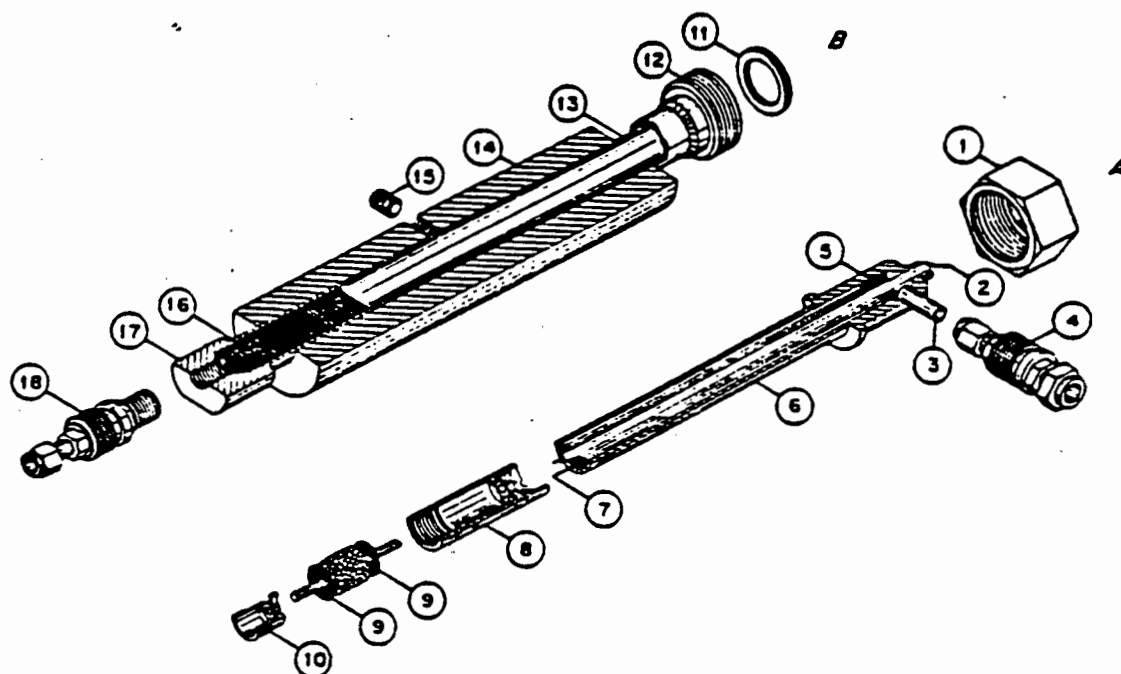
Legend to Figure 2.1:-

A) pressure regulator; B) solenoid valve; C) purification units, D) manually operated needle valve; E) mass flow controller; F) balance; G) pressure gauge with minimum and maximum pressure alarms; H) capped spare liquid feed inlet; I) Lewa pump; J) pressure relief valve; L) 60 micron filter; M) quick connector; N) reactor; O) pressure gauge; P) back pressure regulator; Q) gas sampling valve; R) condenser; S) bubbler; T) wet gas meter; Tc) thermocouple.

For propene and 1-butene feeds a slightly different system was used. The LPG cylinder containing the propene or 1-butene was placed on a balance. From here the feed passed over a 7 micron filter to a Lewa high pressure diaphragm pump which enabled the operating pressure, as set by the back pressure regulator, to be reached.

To prevent cavitation the pump head was cooled to 0°C with an ethylene glycol/ethanol mixture. In addition, the LPG cylinder used to store the feed was modified and fitted with a dual valve, one for liquid and one for gas. On the gas side, an overpressure of nitrogen was maintained thus keeping the propene or 1-butene in the liquid phase. From the pump the feed flow was the same as that for ethene except that no mass flow controller was used. Flow control was managed by checking the weight loss of the cylinder and adjusting the pump settings accordingly.

The reactor used in the above system has been fully described previously⁵⁷ and is shown in Figure 2.2.



Inner tube A

1. Nut, M42 x 2, SS316
2. Thermocouple well, 240 x 2.2 mm id, SS EN58E
3. Inlet tube, 25 x 4.2 mm id, SS EN58E
4. Quick connector, Swagelock-pat'd QF4-B/S, SS316
5. Wire basket, SS316
6. Inner tube body, 227 x 18 mm id, SS316
7. Heat exchanger tubes, 190 x 1 mm id, SS EN58E
8. Catalyst chamber, 30 x 18 mm id, SS316
9. Screen, 100 mesh, SS316
10. Adjustable support plate, 17 x 16 mm id, SS316

Outer tube B

11. Helico flex seal, HN 220, 24.9 mm id, 3.3 torus inconel/nimonic, Joints fargère industrie
12. Outer tube head, 22 x 22.5 mm id, top recess 31.5 x 2.5 mm deep, M42 x 2 thread outside SS316
13. Outer tube body, 230 x 22.5 mm id, SS316
14. Heatsink, 203 mm x 68 mm od x 26.8 mm id, copper
15. Grub screw, M8 x 1.25
16. Wire mesh, Düren-RL, MW = 0.20 mm, DR = 0.13 mm, SS316
17. Reactor bottom, 53 x 16 mm id, SS316
18. Quick connector, Swagelok-pat'd QF-B/S, SS316

Figure 2.2 : Micro-reactor used for catalyst testing

A second inner tube with a smaller catalyst chamber of 12 x 18 mm i.d. was used when the amount of catalyst to be tested was less than 1,5g.

2.1.2. BENCH SCALE SYSTEM

A bench scale system was used to generate litre quantities of product for fuel characterisation tests. Feed and product flow was basically

the same as that for the micro-reactor system, the main difference being that after the reactor the product was distilled on line into petrol and diesel range material.

The reactor used in this system was manufactured at the workshop of the Catalysis Programme at the CSIR. It consisted of a 750mm long stainless steel tube (15,80mm i.d.) equipped with 10 thermocouples equally spaced along the length of the reactor. The thermocouples were used to accurately monitor the reactor temperature before, within and after the catalyst bed which contained up to 40 g of catalyst. The tube was surrounded by an aluminium jacket (80mm o.d.) which acted as a heat sink.

2.1.3 SLURRY REACTOR SYSTEM

Product was also obtained using a slurry reactor system which was being used in a parallel project to generate kinetic data on the oligomerization reaction⁵⁸. Figure 2.3 shows the layout of the system. The advantages of using a slurry reactor are that temperature profiles are absent, therefore the set temperature will be the temperature at which the catalyst is operating.

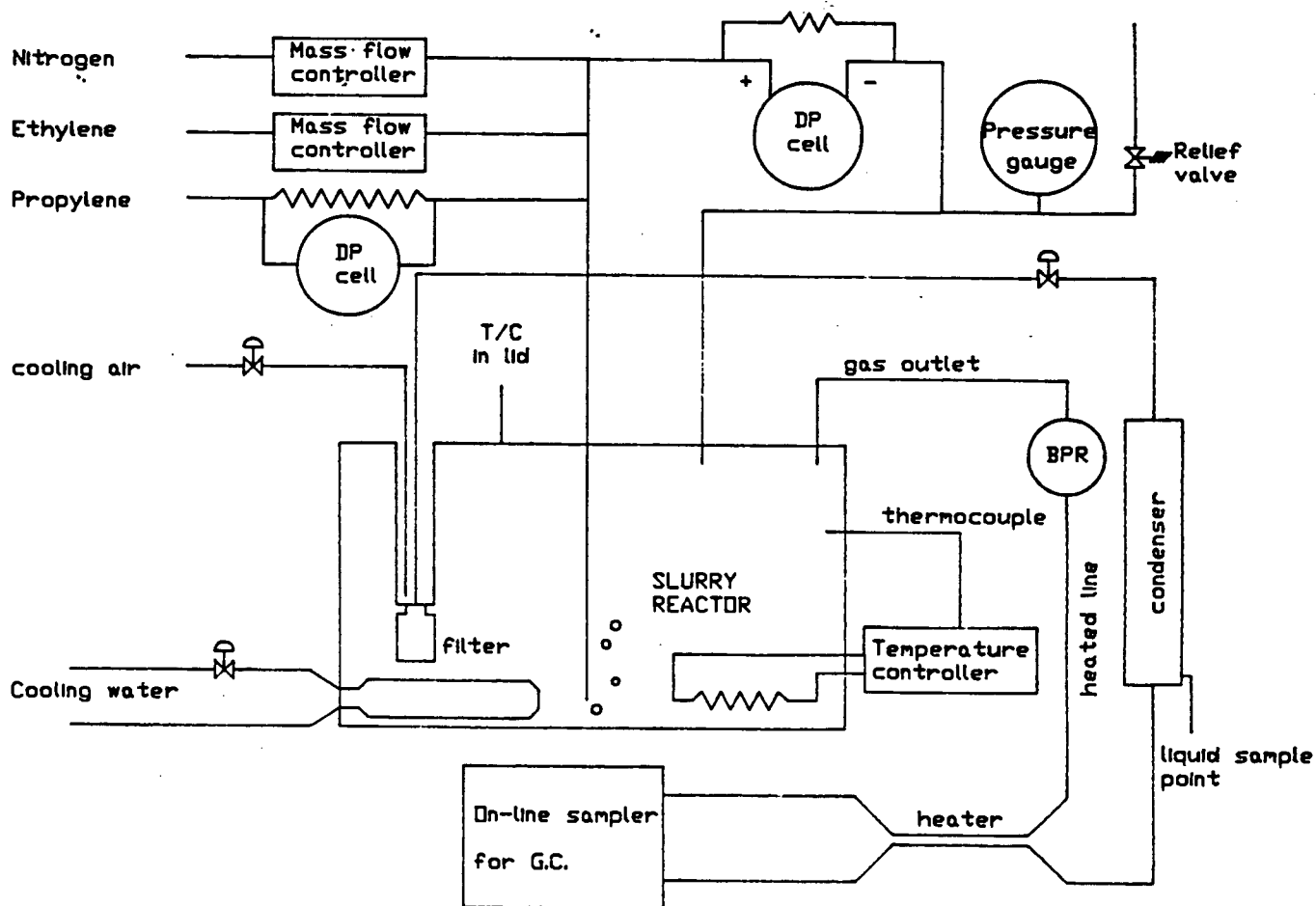


Figure 2.3: Slurry reactor system layout

2.2 CATALYST

The catalyst used in the experiments, unless otherwise stated, was a nickel catalyst supported on silica/alumina made according to SA patent no. 87/9191.

2.2.1 CATALYST ACTIVATION AND OPERATING PROCEDURE FOR THE MICRO-REACTOR

Catalyst was sized to 150 to 300 μm and placed in the catalyst chamber of the reactor which in turn was sealed and placed in the micro-reactor system. The system was pressurised with nitrogen to operating pressure

to check for leaks. On passing this check the reactor was depressurised and the catalyst activated. The catalyst was activated *in situ* by passing nitrogen at a volume hourly space velocity (VHSV) of 1000 over the catalyst at 300°C for 4 hours after which the heat to the reactor was switched off and the catalyst allowed to cool to room temperature. The catalyst had to cool to room temperature because if the feed was passed over newly activated catalyst at elevated temperatures, temperature runaways were experienced. On reaching room temperature the nitrogen flow was switched off and the feed flow was switched on. The feed was allowed to flow over the catalyst for 20 minutes to purge nitrogen remaining in the system. The operating pressure was then set. On reaching operating pressure the catalyst was monitored with regards to overall feed conversion and conversion to diesel range products.

2.3 PRODUCT ANALYSIS

All the product examined in this study was obtained from oligomerization experiments which were carried out at a pressure of 35 bar unless otherwise state.

2.3.1 GAS CHROMATOGRAPHY

The product was analysed on a routine basis using a Carlo Erba model 4300 gas chromatograph (GC) fitted with a flame ionisation detector and a 50m capillary column from Scientific Glass Equipment (SGE). The stationary phase was a dimethyl silicone (BP1) equivalent to SE30 or

diesel range products using a cut-off temperature of 165°C or 180°C. The coolant used in the condenser was water so dissolved gases did not condense and were vented to the atmosphere.

2.3.3.2 Hydrogenation

The diesel product obtained by distillation was hydrogenated using a two litre Parr model 4522 bench top reactor equipped with a Parr model 4841 temperature controller. The catalyst used was a 5% palladium on charcoal catalyst, type 87L, supplied by Johnson Matthey Chemicals as a paste. The reaction was monitored by measuring the bromine number of the product⁵⁹ using IP test method 126 which gives an idea of the degree of unsaturation remaining. No skeletal isomerisation occurred during this treatment.

For estimating the cetane number of the small samples of diesel range product obtained from the micro-reactor system, the total product was hydrogenated before being separated by distillation. In this case the hydrogenation apparatus used was a 200 ml autoclave from Labortechnik.

2.3.4. Physical test methods

The physical testing of the product was performed in accordance with the relevant test methods as prescribed in the SABS specification for diesel fuel. The tests carried out were distillation, and measurements of density, and cetane number. The latter test was performed by the South African Bureau of Standards (SABS) and in some instances by SASOL. The

SABS was used in preference to SASOL because they could report cetane numbers below 35,2, the lower limit for SASOL.

CHAPTER THREE

RESULTS

3.1 FEED CONVERSION

Figure 3.1 shows typical conversion versus temperature profiles obtained for ethene, propene and 1-butene feeds over the supported nickel catalyst. It can be seen from this figure that for C_2 (ethene) high conversions are realised over the full temperature range tested. Figure 3.2 shows the amount of C_{10}^+ product formed over the same temperature range. These results show that higher temperatures favour the production of the C_{10}^+ fraction for all feeds. The optimum temperature for maximising this yield would appear to be in the 200-260°C range. However, these results do not give an indication of the ignition quality of the diesel range fuel produced and in this regard a cetane number correlation method was developed.

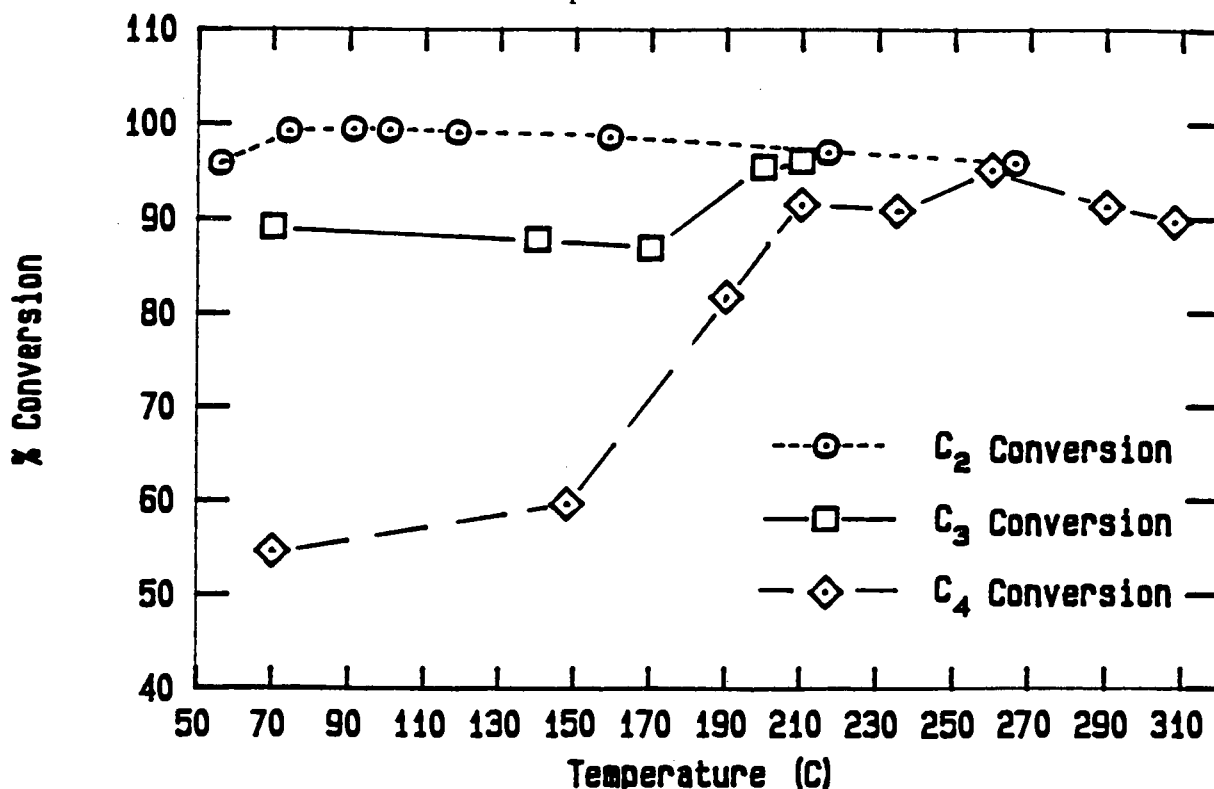


Figure 3.1: % Conversion vs Temperature

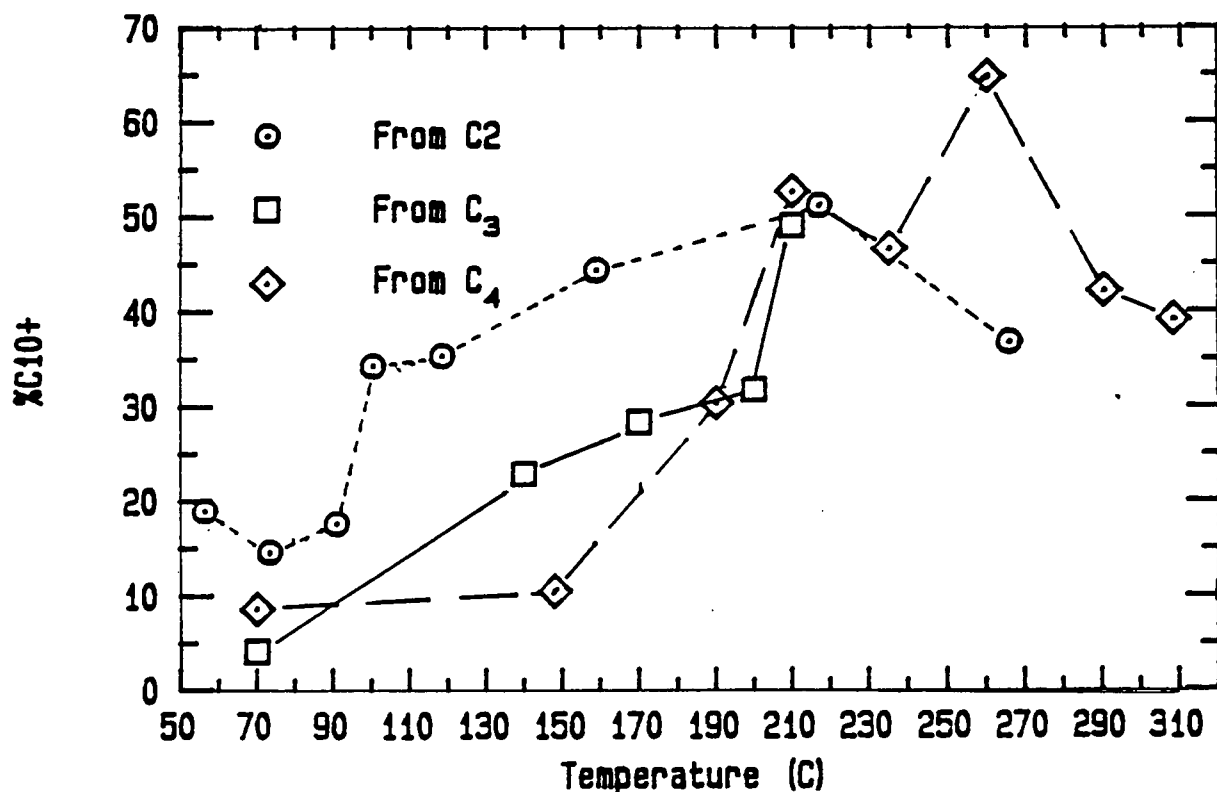


Figure 3.2: % C10+ vs Temperature

Initially, 12 samples of distillate were tested for cetane number at SASOL. 8 of these samples were obtained from the bench scale reactor using a propene feed at temperatures ranging from 100 to 240°C. Two samples were obtained from the slurry reactor using an ethene feed at temperatures of 140°C and 200°C and two samples were obtained from the bench scale and micro-reactor systems using a 1-butene feed. All the cetane numbers of these samples were reported as less than 35,2. Because the cetane number figures were not specific they could not be used in the data base of a cetane number prediction method.

Micro-reader studies indicated that higher cetane numbers should be expected when using an ethene feed. A further 12 samples of distillate were manufactured using ethene as feed and the cetane numbers of the

hydrogenated product were determined at the SABS. The SABS was used for these samples because they can report cetane numbers as low as 25. The results obtained are given in Table 3.1.

Table 3.1: Fuels Data

Sample	Feed	WHSV*	Temp(°C)	Reactor	Cetane No
1	C2	2	120	Micro	51.8
2	C2	3	120	BS	44.9
3	C2	8	120	Slurry	39.0
4	C2	3	180	BS	37.8
5	C2	2	120	BS	36.3
6	C2	2	120	Slurry	35.7
7	C2	2	140	BS	34.5
8	C2	8	160	Slurry	34.7
9	C2	2	160	BS	35.5
10	C2	2	200	Slurry	33.8
11	C2	4	160	Slurry	33.4
12	C2	1	160	BS	29.4

* WHSV = weight hourly space velocity

From Table 3.1 it can be seen that the cetane number of the fuels varies with the type of reactor and the reaction conditions used in their production.

3.2 CETANE NUMBER CORRELATION

It has been stated that ASTM method D976 is not suitable for predicting the cetane numbers of synthetic diesel fuels. This is confirmed in Figure 3.3 where the cetane indices of a number of samples from Table 3.1 were determined and plotted against their measured cetane number. It is readily apparent that ASTM D976 is not suitable for predicting the cetane number of these fuels and that an alternative method is required.

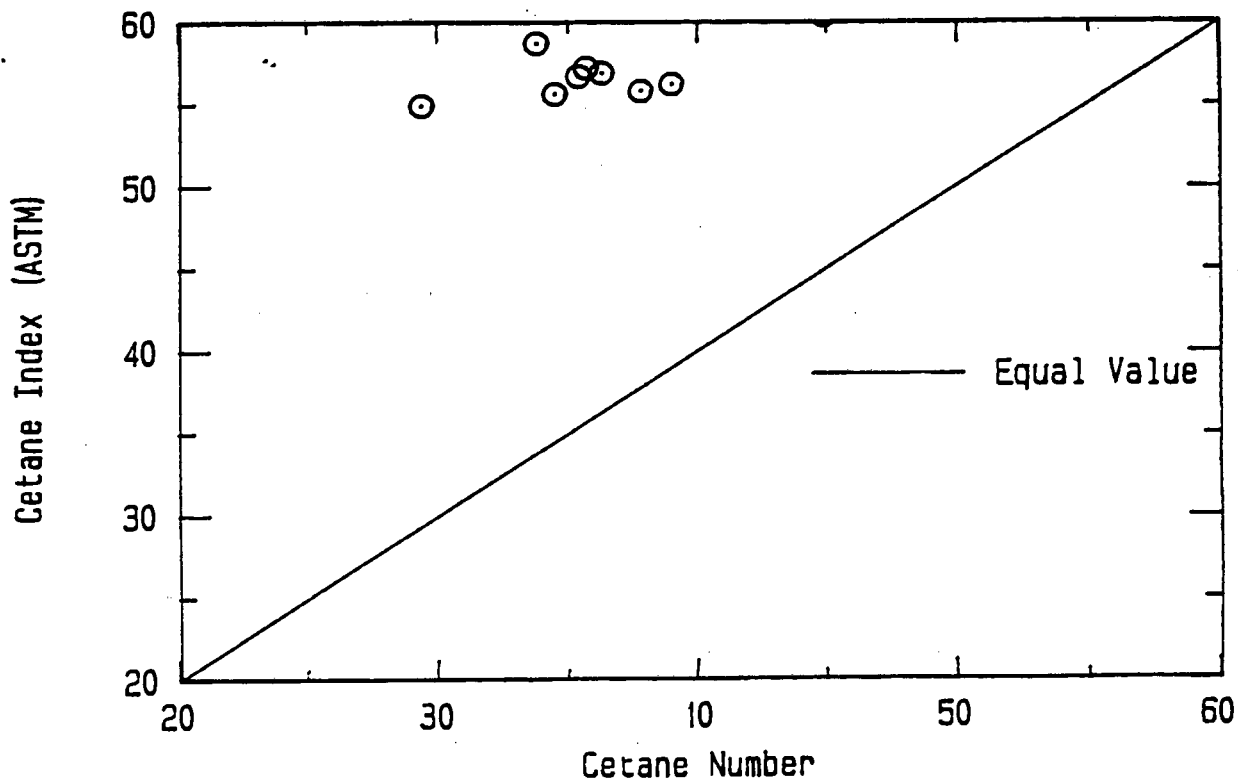


Figure 3.3: ASTM Cetane Index

3.2.1 NMR

Samples 1 to 12 from Table 3.1 were analysed by ^1H NMR and the $\text{CH}_2:\text{CH}_3$ (linear to non-linear) ratio determined.

The correlation was based on the NMR spectra of the hydrogenated fuels because the interpretation of the hydrogenated product spectra is far simpler than that of the unhydrogenated spectra since chemical shifts caused by alkene groups are not present. This can be seen by examining Figure 3.4 and 3.5.

As a comparison, the ^1H spectrum of a commercially obtained diesel fuel is shown in Figure 3.6. The chemical shifts between 6,5 and 8 are caused by aromatic groups. The low percentage of aromatics present suggests that the diesel fuel originated from SASOL.

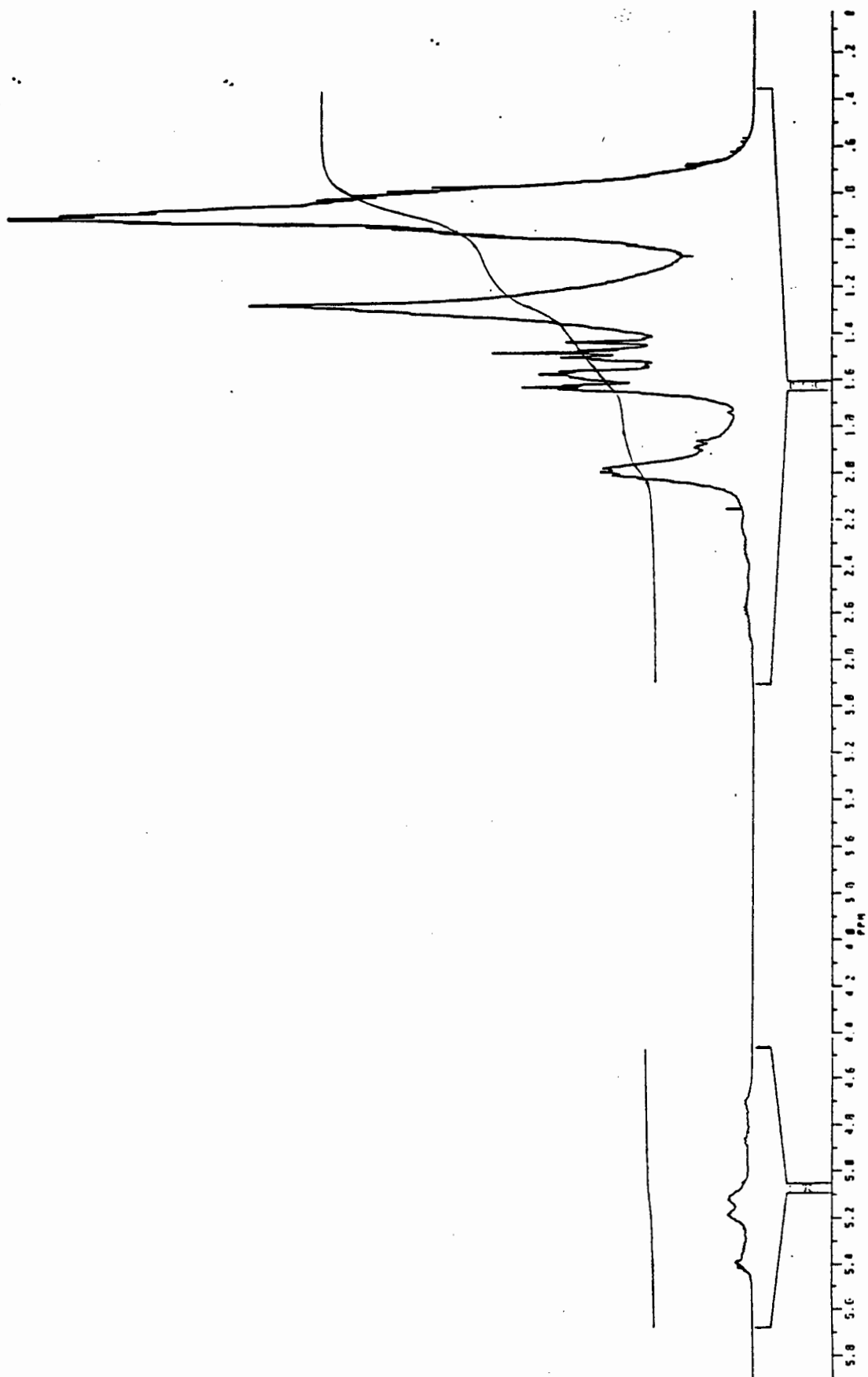


Figure 3.4 ^1H NMR spectrum of unhydrogenated diesel oligomer

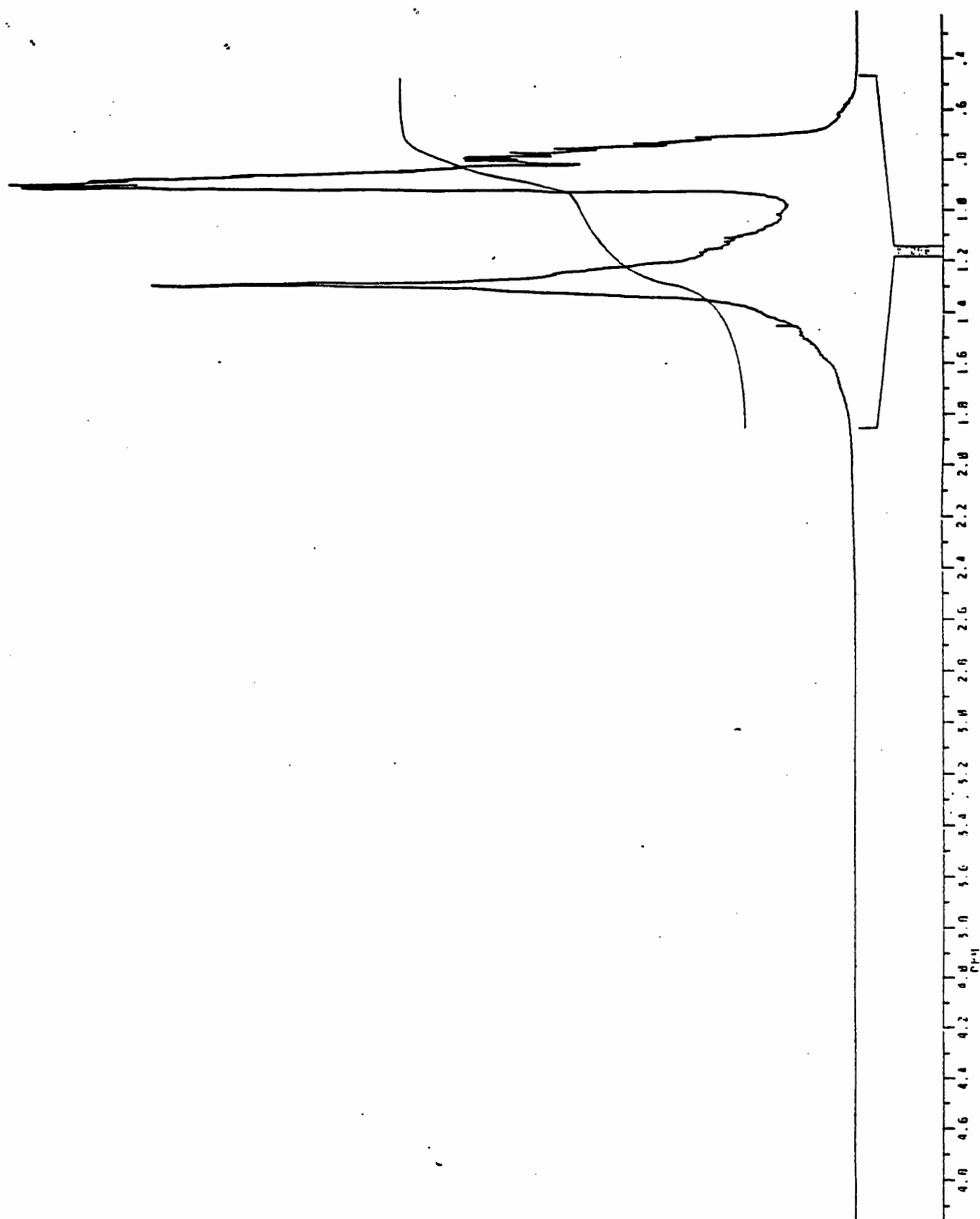


Figure 3.5: ^1H NMR spectrum of hydrogenated diesel oligomer

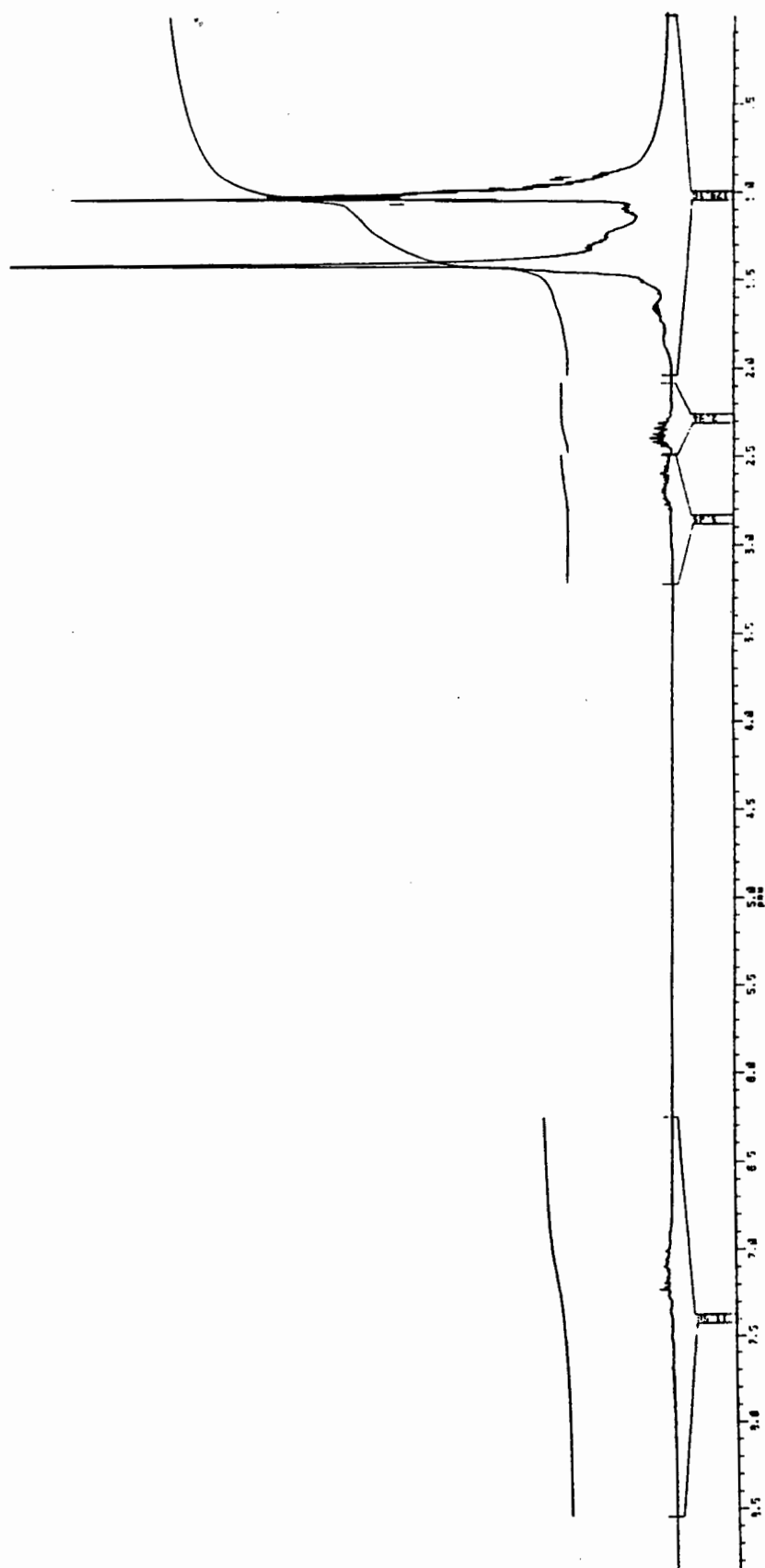


Figure 3.6: ^1H NMR spectrum of a commercial diesel fuel obtained in Pretoria

The ^1H NMR results obtained with samples 1 to 12 enabled Table 3.2 to be drawn up.

Table 3.2: Fuel sample results

<u>Sample</u>	<u>Cetane Number</u>	<u>$\text{CH}_2:\text{CH}_3$ ratio</u>
1	51.8	1.371
2	44.9	1.225
3	39	1.034
4	37.8	1.000
5	36.3	0.969
6	35.7	0.946
7	35.4	0.952
8	34.7	0.923
9	34.5	0.846
10	33.8	0.839
11	33.4	0.921
12	29.4	0.802

From these results it can be seen that a high $\text{CH}_2:\text{CH}_3$ ratio corresponds with a high cetane number. The difference between the ^1H NMR spectra of fuels with high and low cetane numbers (samples 2 and 12) can be seen from Figure 3.7.

It can be seen from this figure that the CH_2 peak decreases as the cetane number decreases. Figure 3.8 shows these results graphically. A linear regression analysis of the results yielded a relationship of the form:

$$\text{PCN} = 2.34 + 35.4 \cdot \text{CH}_2 / \text{CH}_3 \quad R^2 = 0.9627 \quad 3.1$$

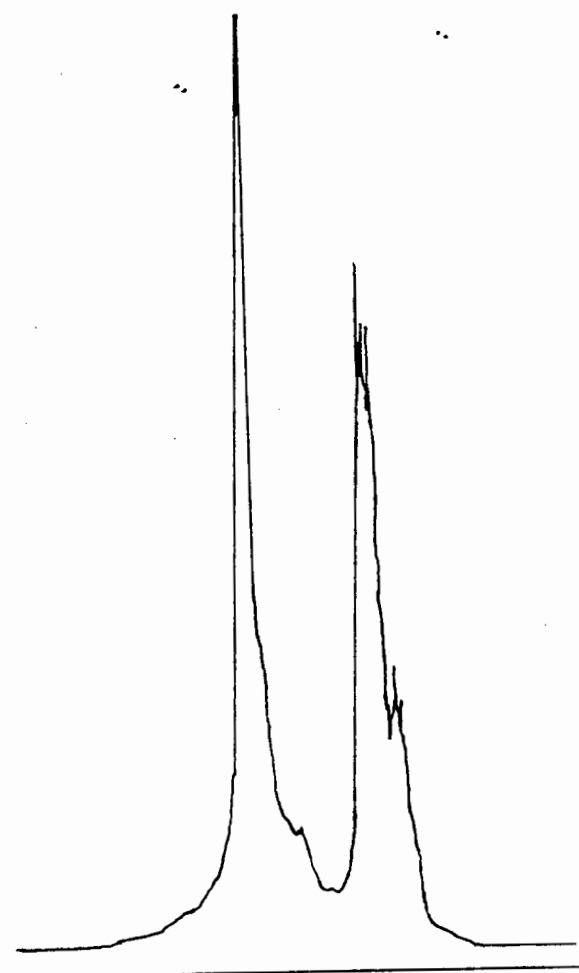
where

PCN = measured cetane number

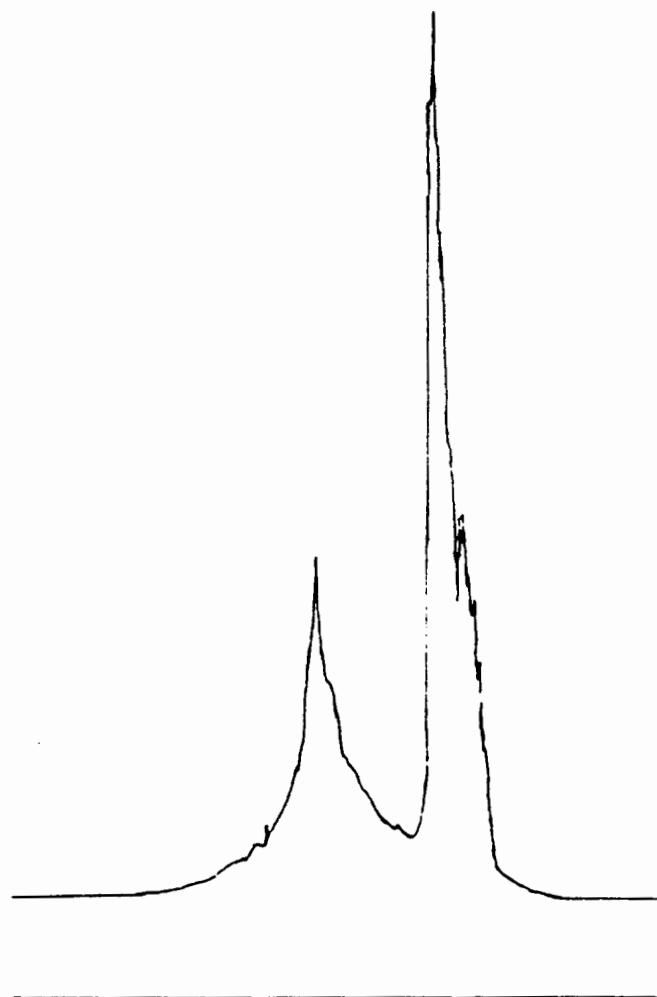
CH_2 = alkane CH and CH_2

CH_3 = alkane CH_3

and R = correlation coefficient



Sample 2
Cetane Number = 44,9



Sample 12
Cetane Number = 29,4

Figure 3.7: ¹H NMR spectra of high and low cetane number fuels

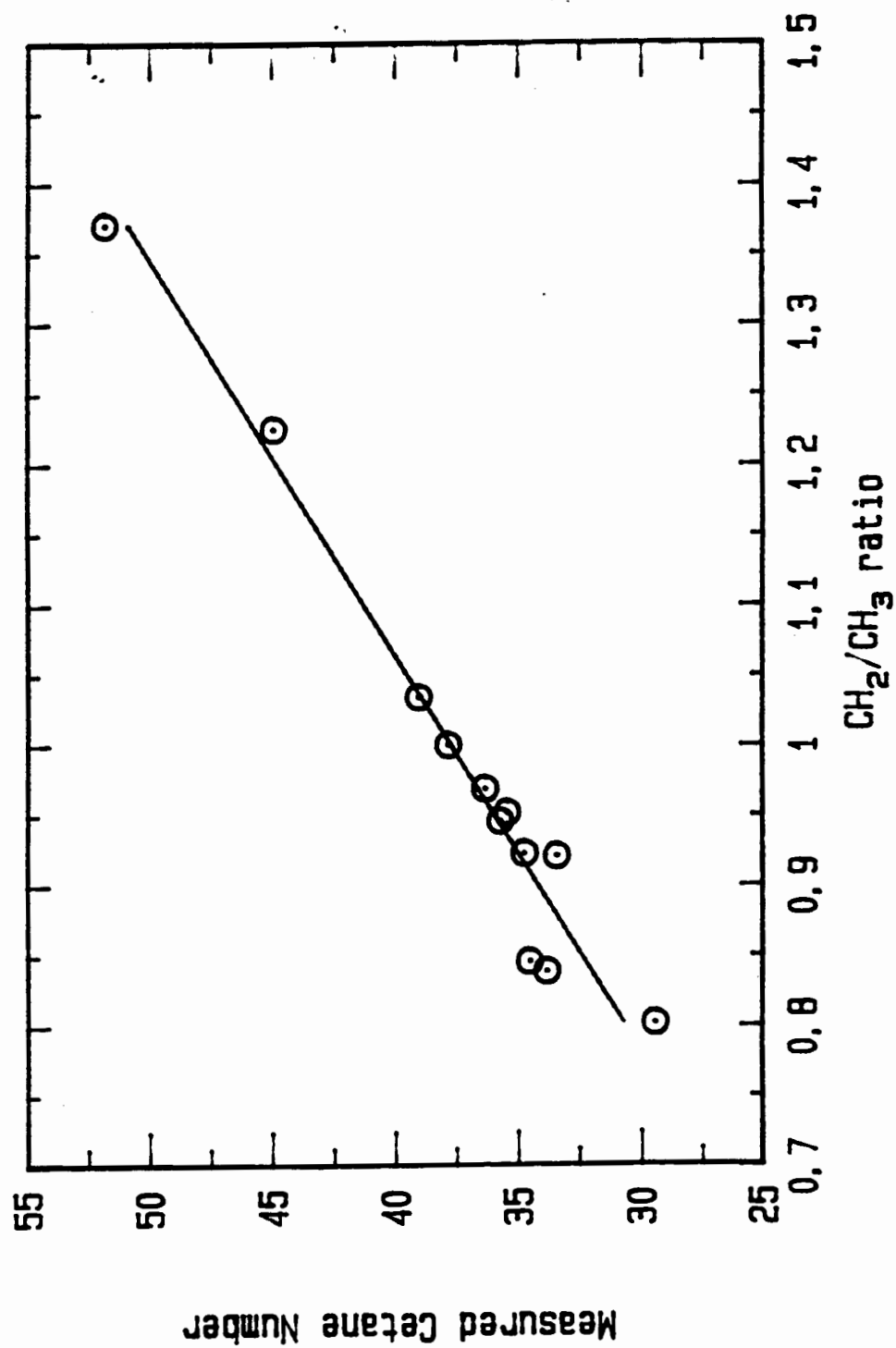


Figure 3.8: Cetane number as a function of CH_2/CH_3 ratio

Although equation 3.1 will accurately predict the cetane numbers of samples which fall within the upper and lower limits of the samples used in the data base (i.e. samples having cetane numbers from 51, 8 to 29,4), it should not be expected to accurately predict the cetane numbers of samples which fall outwith these limits. For example, the predicted value for cetane using the above equation would be 167,6.

Therefore, to extend the range of the cetane number prediction equation the $\text{CH}_2:\text{CH}_3$ ratios of the n-alkanes and two highly branched alkanes (HMN and 2,3,4,6,6-pentamethylheptane), representing the two extremes of the cetane number scale, were calculated (see Table 3.3). These values were added to those obtained with the synthetic diesel fuels and Figure 3.9 was drawn up. The values for the cetane numbers of the pure compounds were obtained from Rose and Cooper⁶⁰.

Table 3.3: CH_2/CH_3 ratios of various pure compounds

<u>Hydrocarbon</u>	<u>CH_2/CH_3</u>	<u>Cetane Number</u>
(C12H26) Pentamethylheptane	0,238	9
(C16H34) Heptamethylnonane	0,259	15
(C 7H16) Heptane	1,667	56
(C10H22) Decane	2,667	76
(C12H26) Dodecane	3,333	80
(C13H28) Tridecane	3,667	88
(C14H30) Tetradecane	4,000	93
(C15H32) Pentadecane	4,333	95
(C16H34) Hexadecane	4,667	100
(C17H36) Heptadecane	5,000	105
(C18H38) Octadecane	5,333	110

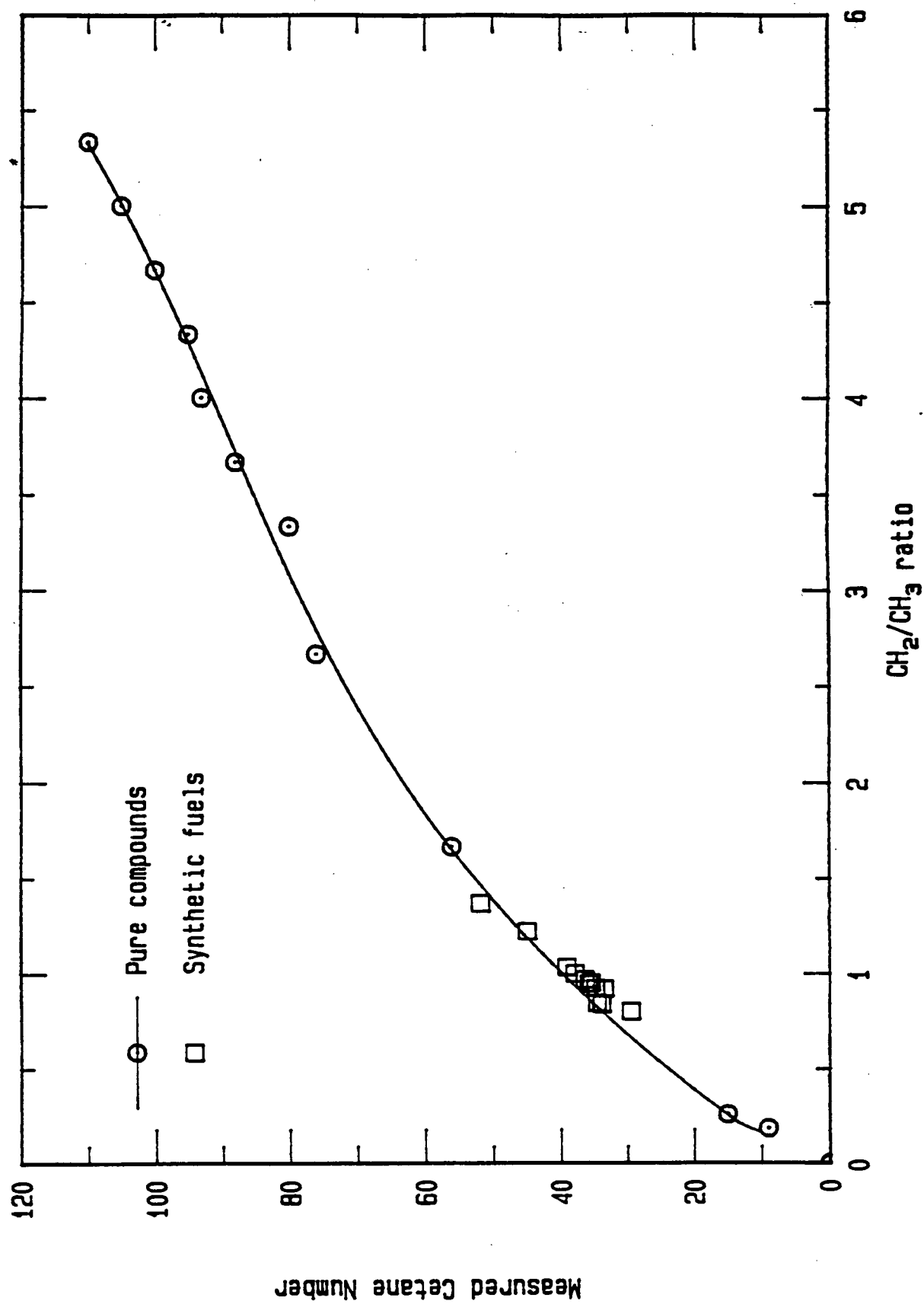


Figure 3.9: Cetane number vs CH_2/CH_3 ratio of pure compounds

As can be seen, the relationship is not linear with the following expression being obtained:-

$$\text{PCN2} = 1.8 + 43.8(\text{CH}_2/\text{CH}_3) - 8.1(\text{CH}_2/\text{CH}_3)^2 + 0.69(\text{CH}_2/\text{CH}_3)^3$$

$$R^2 = 0.9977 \quad (3.2)$$

Using samples 1 to 12 of Table 3.1, the two derived cetane number prediction formulae (equations 3.1 and 3.2) were compared in Table 3.4 with the prediction methods of Gautier (equation 1.17) and Pande and Hardy (equation 1.13).

Table 3.4: Comparison of cetane number prediction formulae

Sample	Cetane No.	PCN1	PCN2	Gautier	Pande/Hardy
1	51,8	50,9	48,4	51,6	56,8
2	44,9	45,7	44,6	48,9	53,6
3	39,0	38,9	39,2	44,7	48,7
4	37,8	37,7	38,2	43,9	47,7
5	36,3	36,6	37,3	43,1	46,8
6	35,7	35,8	36,6	42,5	46,1
7	35,4	36,0	36,8	42,7	46,3
8	34,7	35,0	35,9	41,9	45,4
9	34,5	32,3	33,5	39,8	42,8
10	33,8	32,0	33,3	39,5	42,6
11	33,4	34,9	35,8	41,8	45,3
12	29,4	30,7	32,1	38,4	41,3

It can be seen from this Table that for the samples tested the two PCN prediction methods are better predictors of cetane number than the prediction methods of either Gautier or Pande and Hardy. Figure 3.10 shows that using method PCN1 all the samples except sample 9 are predicted within 2 cetane numbers and using method PCN2 only samples 1, 11 and 12 are not predicted within 2 cetane numbers. Using Gautiers'

method, all the samples except samples 1 and 2 are overpredicted by at least 5 cetane numbers whilst all the cetane numbers are overpredicted by this margin with the method of Pande and Hardy.

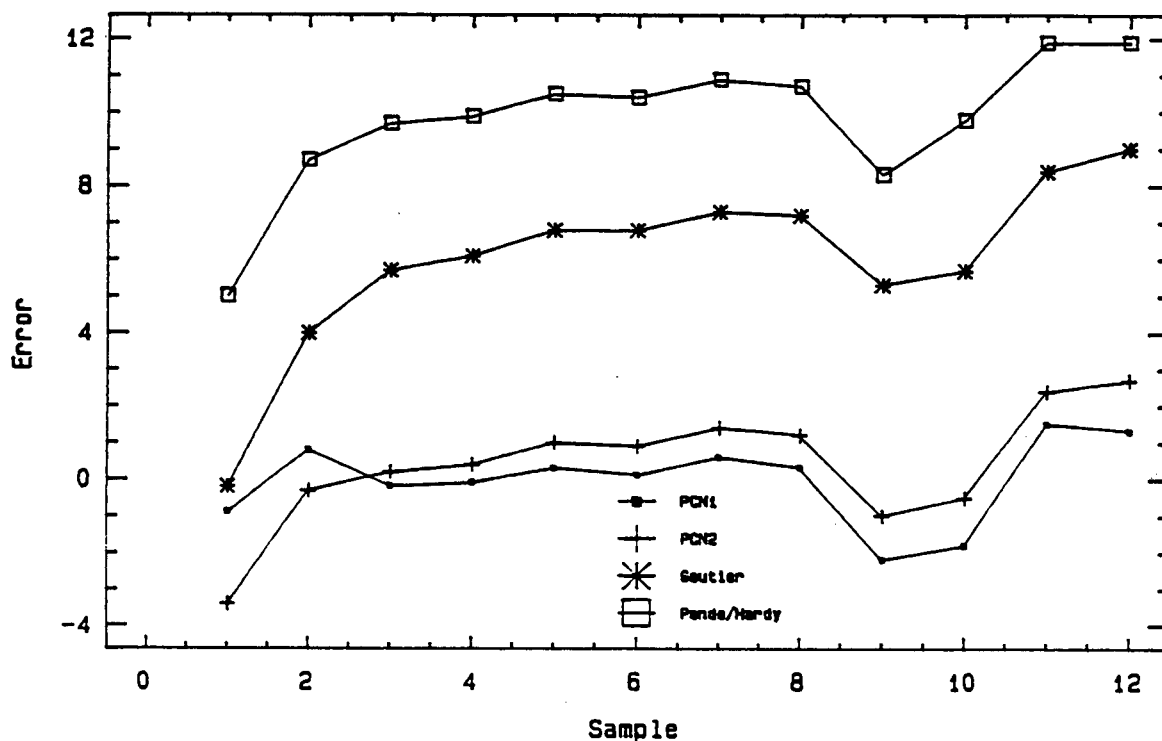


Figure 3.10: Difference between measured cetane numbers and predicted cetane numbers

To test if the derived correlations, PCN1 and PCN2, could accurately predict the cetane numbers of synthetic diesel fuels which were not part of the original 12 fuels used in deriving equations 3.1 and 3.2, the cetane numbers of an additional 6 fuels were determined. The conditions of manufacture and the results obtained with these fuels are given in Table 3.5.

Table 3.5: Test results

Sample	WHSV	Temp, °C	Feed	Reactor	CH ₂ :CH ₃ Ratio	C.No	PCN1	PCN2
13	2	160	C ₂	Slurry	0,874	34,7	33,3	34,4
14	1	120	C ₂	BS	0,904	35,8	34,3	35,3
15	12	160	C ₂	Slurry	0,981	38,6	37,1	37,6
16	2	120	C ₂	BS	1,206	43,8	45,0	44,0
17 *	-	-	-	-	1,400	50,1	51,9	49,1
18 +	2	260	C ₃	Micro	1,012	36,4	38,1	38,5

C.No = Measured cetane number

*Catalyst used was H-ZSM 5. Reaction conditions are not available.

+Catalyst used was Ni-P7H (nickel supported on an amorphous silica-alumina)⁶¹.

It can be seen that the predicted cetane numbers fall within the reproducibility limits of ASTM D613 (Section 1.2.3). These results are of particular interest since samples 17 and 18 originated from different catalyst sources and feedstocks. In addition, sample 18 was found to contain a small amount of aromatics.

3.3 OLIGOMERIZATION REACTIONS

The cetane number prediction equations were developed to estimate the cetane numbers of the small volumes of fuel obtained from catalyst and process development tests. However, prior to continuing with the oligomerization reactions it had been noticed from Table 3.1 that as the WHSV decreased the cetane number decreased (see Figure 3.11).

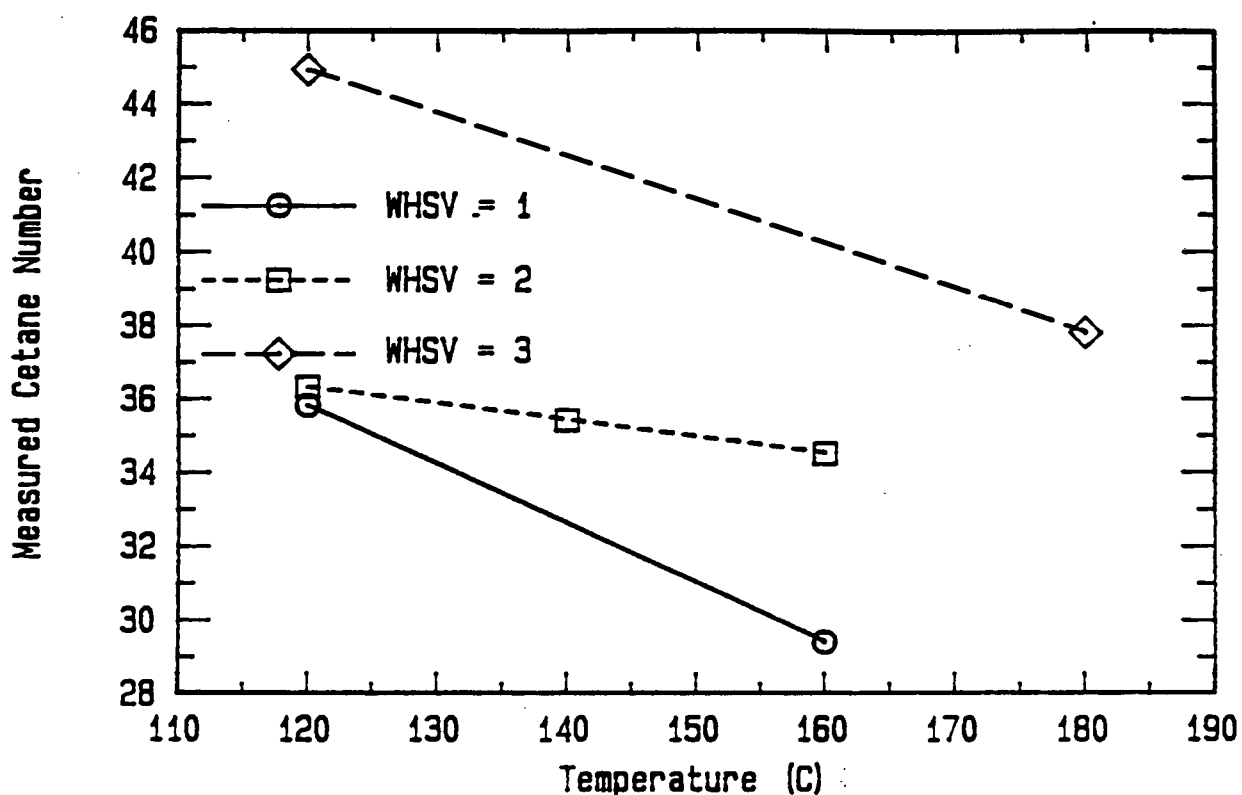


Figure 3.11: Cetane Number vs Temperature at WHSV of 1, 2 and 3

As the WHSV decreases the carbon number should increase because the residence time of the feed on the catalyst is increased. For a diesel fuel derived from crude-oil an increase in carbon number generally results in an increase in cetane number. However, the above results show that for these samples this is not the case. To test this anomaly, the fraction of sample 3 (Table 3.1) which distilled between 165 and 180°C was analysed by ^1H NMR and the following found:-

CH_2/CH_3 ratio - 1,313

PCN1 - 48,8

PCN2 - 46,4

The results from this sample showed that the inclusion of the 165-180°C fraction could be expected to improve the ignition quality of the fuel as a whole. Therefore, for the following samples a cut-off point of 165°C was used.

Having obtained the PCN1 and PCN2 cetane number prediction methods a supported nickel catalyst with a nickel content of 1,33% by mass was used to monitor the effects of pressure, temperature and WHSV on an ethene feed with regards to % conversion, %C10+ formed and cetane number.

3.3.1 EFFECT OF PRESSURE

In Figure 3.12 the % ethene conversion obtained with the micro-reactor at 5 different pressures is shown as well as the %C10+ and the predicted cetane numbers using method PCN1. The WHSV for the reactions was 4g feed/g cat/h and the reaction temperature was approximately 110°C. At pressures below 20 bar no diesel range product was formed. The %C10+ produced actually dropped slightly as the pressure was increased from 20 bar to 50 bar but at the same time the cetane number increased. Despite this increase, the predicted cetane numbers of the fuels were markedly lower than the SABS specification minimum of 45.

Table 3.6 shows the results obtained with the slurry reactor at pressures ranging from 19 to 50 bar. It can be seen that even by varying the WHSV from 2 to 12 g feed/g cat/h that a relatively constant, low cetane number was obtained.

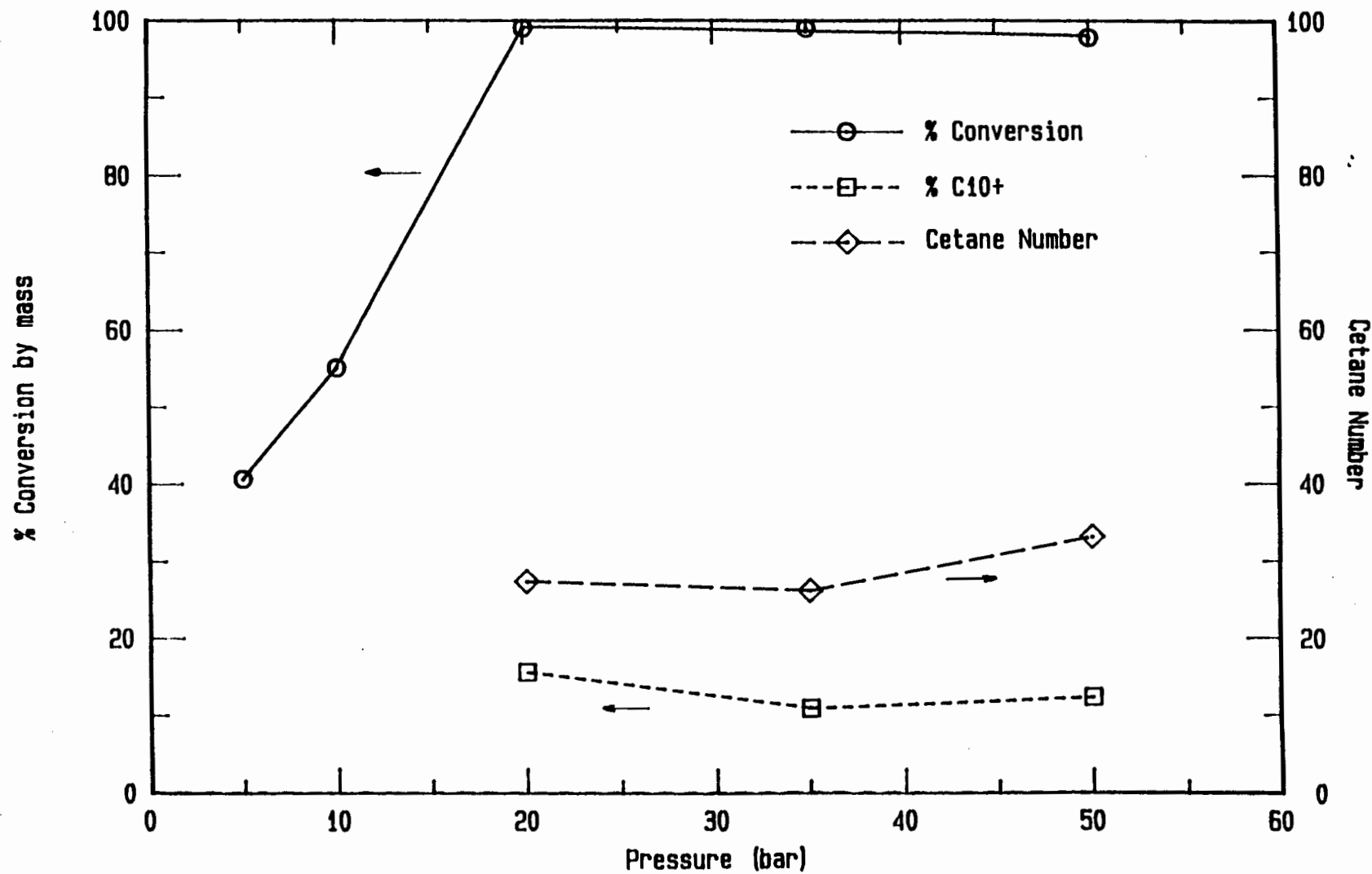


Figure 3.12: Effect of Pressure

TABLE 3.6: Effect of Pressure in the slurry reactor

Pressure (bar)	WHSV	% Conversion	%C ₁₀	PCN ₁
19	2	81,8	18,4	32,2
25	2	92,2	24,3	32
25	8	91,4	13,9	36,8
35	8	93,8	13,4	35
50	12	95,6	20,4	34

The temperature in all cases was 120°C

3.3.2 EFFECT OF WHSV

The effect of WHSV on % conversion, %C₁₀+ and cetane number is shown in figure 3.13. The reaction temperature was about 105°C and the pressure was 35 bar. Again, despite high overall conversions low amounts of diesel range product were produced at all WHSV's. As the WHSV was increased the conversion of ethene decreased from 99,8 to 97,6%. At WHSV's of 2, 4 and 6, the cetane number of the diesel range product remained constant at about 41. At a WHSV of 1 there was a drop in cetane number to 34.

3.3.3. EFFECT OF REACTION TEMPERATURE

Figure 3.14 shows the effect temperature had on the ethene oligomerization reaction. The WHSV was held constant at 4 g feed/g cat/h and the pressure used was 35 bar. It can be seen that as the temperature was increased from 100°C to 255°C the %C₁₀+ increased dramatically from 12,5 to 49,8% by mass. However, at the same time, the cetane number of the diesel range product decreased from 40,2 to 27,3. This decrease in cetane number can be explained by examining the

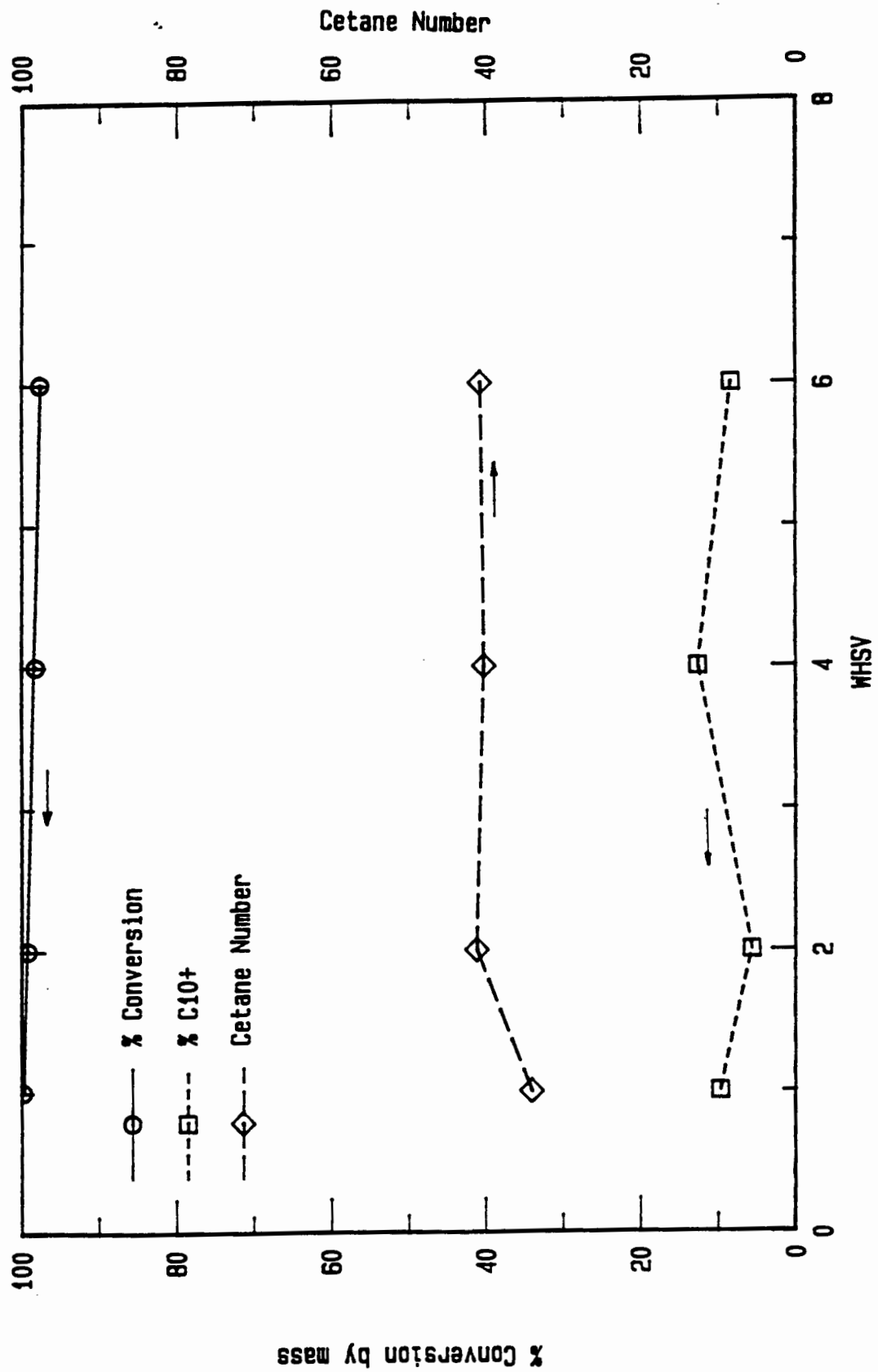


Figure 3.13: Effect of WHSV

effect of temperature on the carbon number distribution of the product. It can be seen from Figure 3.15 that with an increase in temperature there is a distinct activity for the conversion of the primary butene products. This can be seen by comparing the amount of C8 and C6 formed. From 200°C there was more C8 than C6 being produced. An analysis of the distillate fraction of butene oligomerization products obtained from the slurry reactor showed that with an increase in reactor temperature from 100 to 160°C the predicted cetane numbers using method PCN1 decreased from 41,9 to 32,4 respectively. Additionally, samples of ethene oligomer which were formed at 55, 140 and 210°C were hydrogenated and the C₆ fraction analysed by gas chromatography. Because the reaction follows a chain growth mechanism, it was assumed that the products formed in the C₆ fraction would be typical precursors of the higher molecular weight products obtained in the diesel fraction. Therefore the results obtained with the C₆ fraction would be a reflection of what was occurring in the diesel range product. The results obtained are given in Table 3.7.

Table 3.7: Effect of temperature on hydrogenated C₆ product from ethene oligomerization

Compound	% by mass found in sample manufactured at		
	55°C	140°C	210°C
2,3-di-Me-butane	0	0.07	5.26
2-Me-pentane	0.71	2.71	30.09
3-Me-pentane	39.43	40.45	34.66
n-hexane	59.85	56.77	29.99

These results show that there is a significant change in selectivity between 140°C and 210°C with a concurrent increase in the amount of

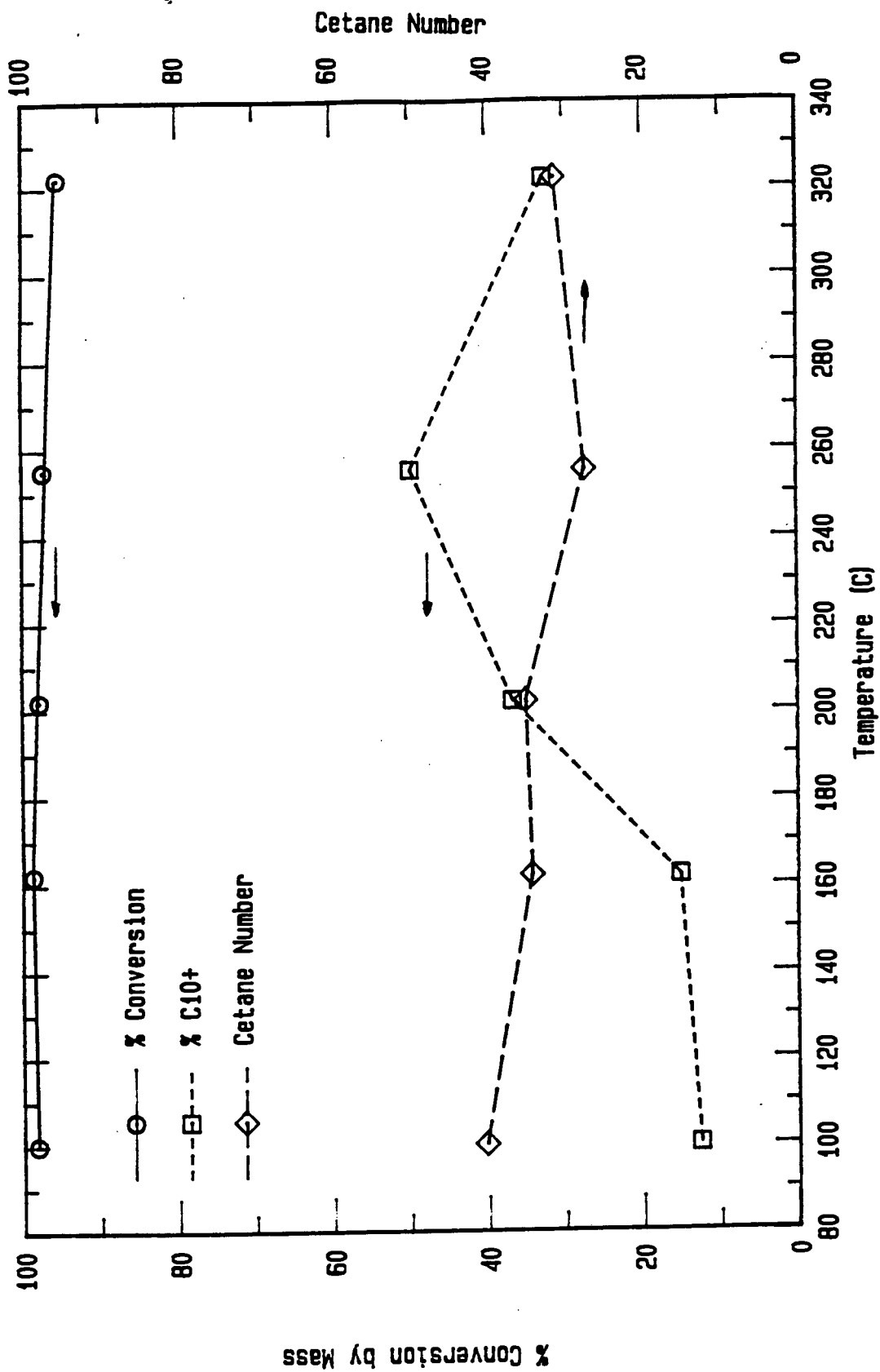


Figure 3.14: Effect of Temperature

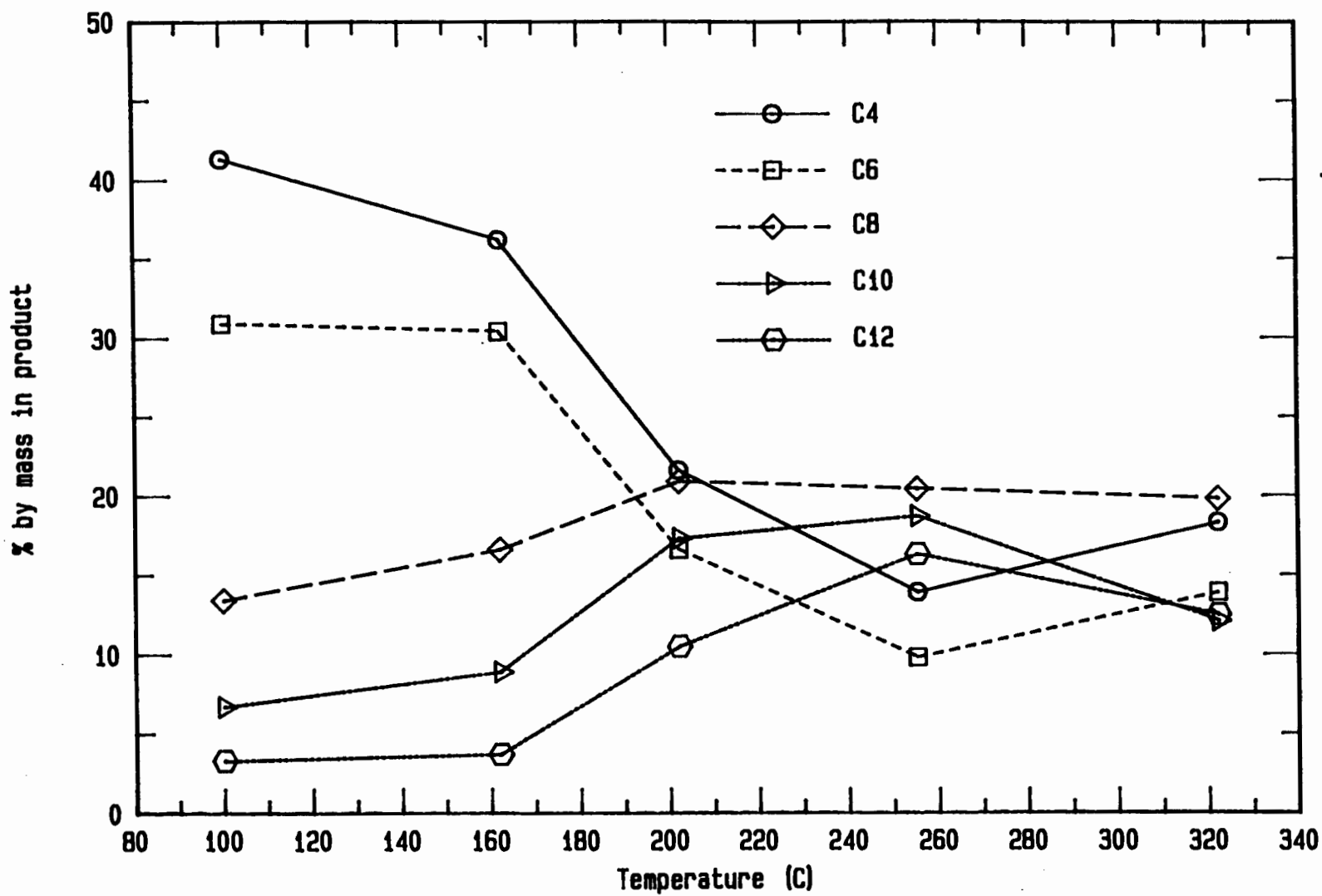


Figure 3.15: Effect of Temperature on Carbon Number Distribution

branched products formed. If there was a similar increase in the amount of branched products formed in the diesel range oligomerization product the result would again be a lower cetane number.

3.3.4 EFFECT OF CATALYST PRETREATMENTS AND MODIFICATIONS

The effect of the various catalyst pretreatments and modifications on the oligomerization of ethene were also studied.

When the catalyst was activated under hydrogen flow instead of nitrogen, no reaction of ethene occurred at 100°C. This showed that the nickel must be present on the catalyst in the form of Ni^{2+} or Ni^{1+} and is reduced to Ni^0 in a hydrogen atmosphere.

The increased activity for butene oligomerization with an increase in temperature could be caused by acid sites on the catalyst. To test this theory the catalyst was base pre-treated with ammonia by passing a mixture of 5cc of ammonia and 45cc of nitrogen over the catalyst for 3 hours. After this time the ammonia flow was stopped and the nitrogen flow continued overnight. The catalyst was then activated under nitrogen flow as usual. It can be seen from figure 3.16 that as the temperature was increased the amount of C_{10+} remained approximately constant. An interesting observation is the decrease in conversion between 120 and 170°C. The predicted cetane number of the product obtained at 80°C was 43,3.

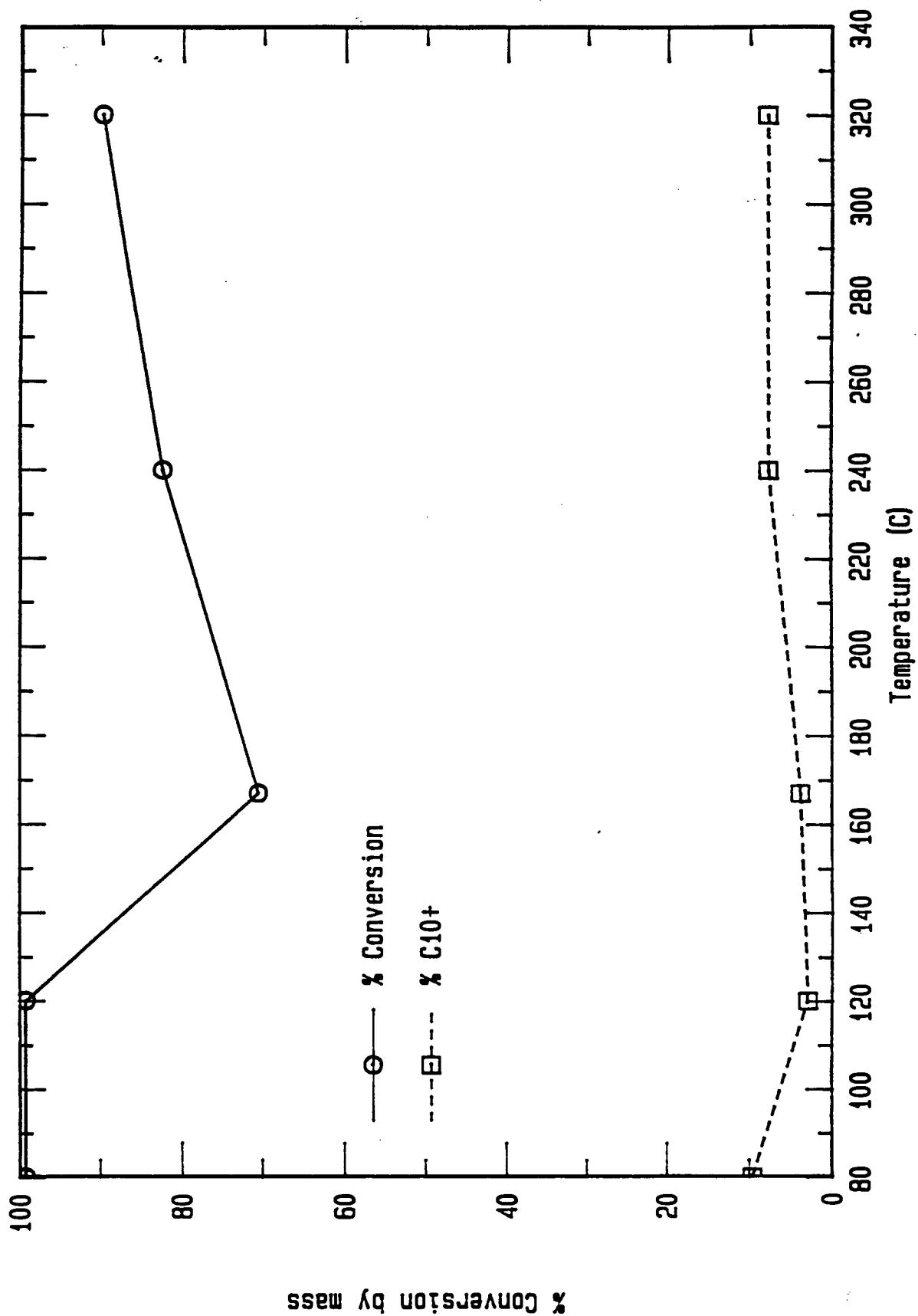


Figure 3.16: Effect of Ammonia Pretreatment

An attempt to convert ethene using nickel supported on a commercial support obtained from Harshaw was also unsuccessful. The reaction was stopped after running for 24 hours at 100°C because no liquid had been formed.

When the supported nickel catalyst was used undiluted, large temperature fluctuations were experienced. To minimise these variations 1g of the nickel catalyst was diluted with 4g of glass ground to the same particle size as the catalyst. The largest temperature variations experienced with this set-up were $\pm 5^{\circ}\text{C}$. Figure 3.17 shows the results obtained graphically. If this figure is compared with figure 3.14 it can be seen that overall the effect of temperature on the oligomerization reaction was the same in both cases.

Similarly, the effect of temperature on carbon number distribution with the diluted catalyst can be seen in Figure 3.18. Again, the overall effect was the same as for the undiluted catalyst (see Figure 3.15) suggesting that the temperature fluctuations do not significantly effect the conversion or diesel range product quality.

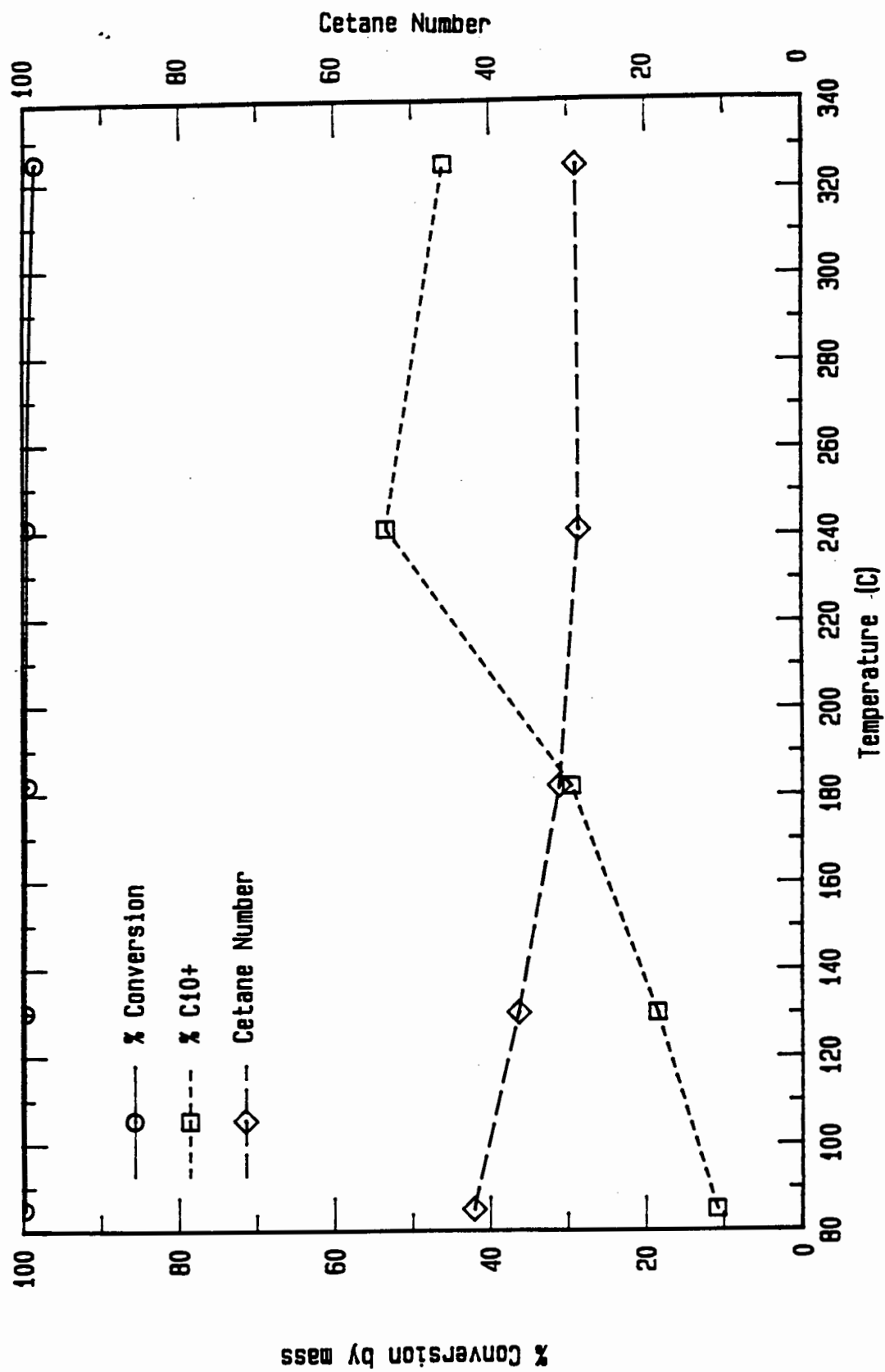


Figure 3.17: Effect of Temperature on Diluted Catalyst

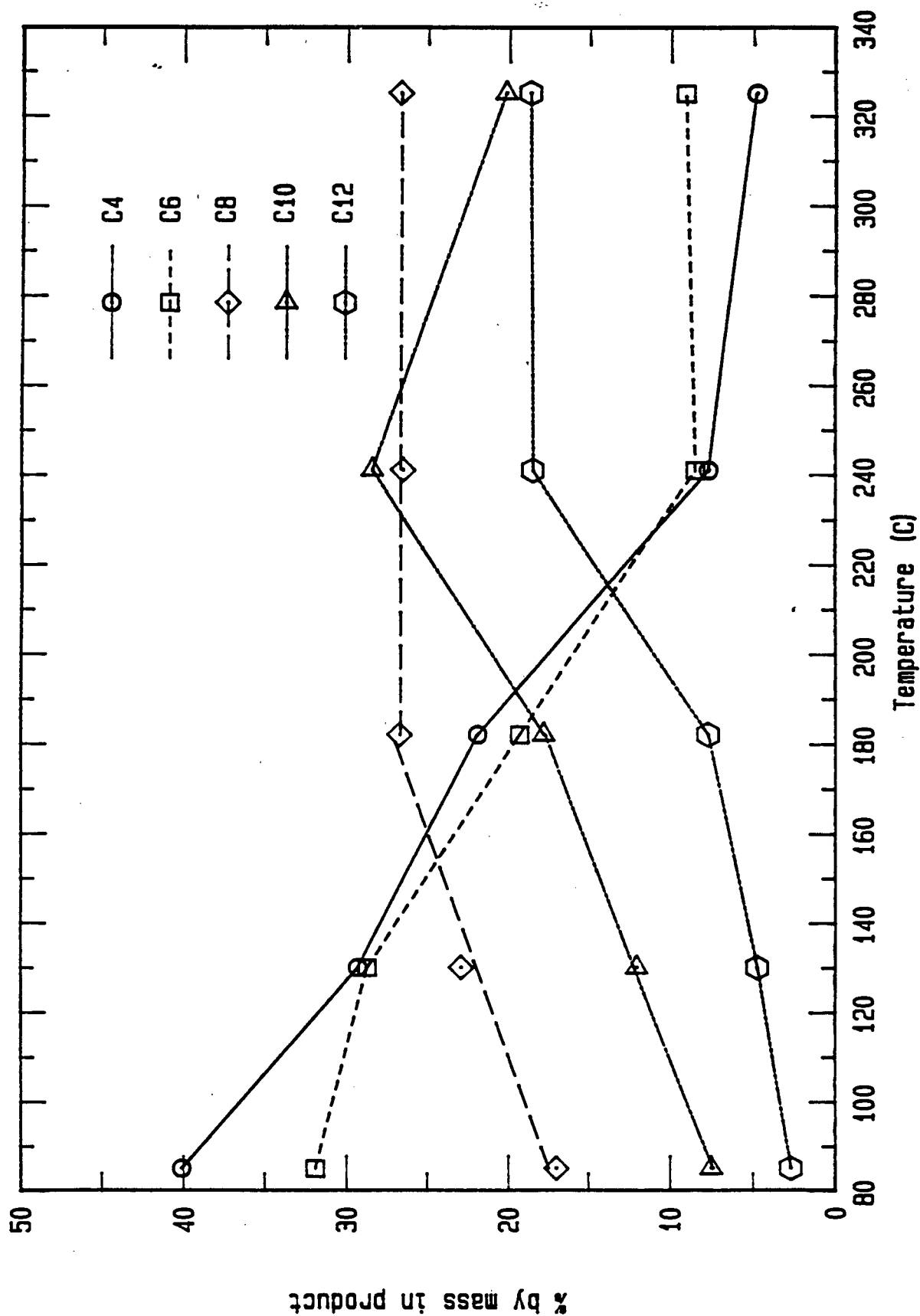


Figure 3.18 Effect of Temperature on Carbon Number Distribution (Dil.Cat.)

CHAPTER FOUR

DISCUSSION AND CONCLUSION

4.1 DISCUSSION

No rapid, reliable, indirect methods exist at present for determining the cetane numbers of synthetic fuels obtained from alkene oligomerization. Use must be made of methods developed for petroleum based diesel fuels which yield doubtful results. This can be seen by examining Figure 3.3 where the cetane numbers of several synthetic diesel fuels used in this study were estimated using ASTM D976 and compared with the values obtained with the engine test. This figure shows that ASTM D976 hopelessly overestimates the cetane numbers. The reason for this is that compared with their crude oil derived equivalents, these synthetic diesel fuels do not contain any aromatic compounds. Conventional diesel fuels contain about 15% aromatics⁶². Thus, the synthetic diesel fuels will have a comparatively low density which, for conventional fuels and the purpose of ASTM D976, is equated with a high cetane number.

It was shown in Section 1.2.3 that cetane number is related to chemical structure with alkanes having the highest cetane numbers and aromatics the lowest. This is because a compression ignition (diesel) engine relies on the spontaneous ignition of the fuel used when injected into the hot, compressed air in the cylinder. Therefore, in general, fuels such as the n-alkanes which have low ignition temperatures (low thermal stability) have high cetane numbers while aromatics have high

spontaneous ignition temperatures (high thermal stability) and low cetane numbers.

Since the hydrogenated synthetic diesel fuels used in this study do not contain any non-alkane species in appreciable quantities, differences in cetane numbers must be caused by differences in the iso-alkane content and the average degree of branching present. The greater the degree of branching the lower the cetane number (c.f. cetane and heptamethylnonane).

Gas chromatography was used routinely to analyse the oligomerization product and is useful for determining carbon number groupings. However, for a meaningful cetane number correlation method more information concerning the average structure of the C10+ fraction as discussed above is required. ^1H NMR spectroscopy was chosen as the most applicable analytical tool because it is capable of obtaining detailed structural information on hydrocarbon mixtures. ^1H NMR was used instead of ^{13}C NMR because it is faster in data acquisition and more available than ^{13}C NMR equipment. In addition, in the study by Gautier⁵⁶ where the use of ^1H NMR and ^{13}C NMR in cetane number correlations were compared, the conclusion was reached that ^{13}C NMR did not possess any operational advantages over ^1H NMR. Also, it is unlikely that the oligomerization products obtained for analysis will contain many, if any, quaternary carbon groups. Therefore a ^{13}C NMR spectrum will not give any more information relevant to this study which cannot be obtained from a ^1H NMR spectrum.

The cetane number correlations were based on the hydrogenated synthetic diesel fuels because in an industrial application the product would be hydrogenated to improve the storage stability of the fuel and to increase the cetane number since cetane number is directly proportional to the hydrogen content⁶³. Furthermore, as shown in Figures 3.4 and 3.5 the interpretation of the hydrogenated product spectra is far simpler than that of the unhydrogenated spectra since chemical shifts caused by alkene groups are not present. With the exception of sample 18, the NMR spectra also confirmed that the synthetic oligomers did not contain any aromatic compounds because no signals were recorded in the 6-8ppm region of the spectra.

Initially doubts were expressed as to whether a CH_2/CH_3 ratio could be used to predict cetane number since the cetane numbers of pure compounds varied inconsistently with branching⁶⁴. For example, 4-propyldecane has a lower cetane number than 2,5-dimethylundecane (39 and 58 respectively)⁶⁰ despite having a lower degree of branching. Similarly, 8-propylpentadecane (48) has a lower cetane number than 7,8-diethyltetradecane (67). However, the above cetane numbers were actually calculated from cetene number results³⁶ according to the equation: Cetane number = $0,875 \times \text{cetene number}$. In turn, these cetene numbers were calculated from the results obtained with a static bomb thus errors in the relationships between each method will be compounded. Pucket and Caudle themselves point to significant disagreements between the cetane and cetene number scales and conclude that predicting ignition qualities from scanty information is fallacious. Also, there were no cases of an iso-alkane having a higher cetane number than its

corresponding n-alkane. It was therefore felt that differences in the cetane numbers of the hydrogenated C10+ fraction of the oligomers, which in reality is a complex mixture of a large number of different hydrocarbons, could only be caused by differences in the average amount of branching occurring.

The amount of CH_3 groups present, as determined from the ^1H NMR spectra can be treated as a measure of the average degree of branching present in the fuel sample. Similarly, the amount of CH_2 groups present represents the average degree of linearity of the fuel. Since this is an average, in cases where CH_2 groups are present in ethyl etc. side chains, the CH_2 will still be included as part of the linear portion of the sample. There is not enough information in the literature regarding the engine testing of pure hydrocarbons to say whether this means that the prediction equations give a "best" value or not.

As discussed in section 1.2.4, an increase in the degree of branching of an alkane tends to reduce the cetane number. It would therefore be expected that the CH_3/CH_2 ratio, which is called the branching index (BI)⁶⁵, would correlate with the cetane numbers of the fuel. Table 3.2 shows that this is in fact the case. The inverse of the BI (CH_2/CH_3 ratio) was used so that a high value is representative of a high cetane number.

The limitations of the correlation derived stem from the relatively small number of fuels used in the data base. It would have been desirable to include a larger number of fuels especially in the 40 to 60

cetane number region. It is unlikely that the correlation derived will accurately predict the cetane numbers of diesel fuels with cetane numbers lying outside the high and low values of the fuels used in the data base. For example the predicted value for cetane using the PCN1 method is 167,6.

Errors in obtaining the NMR data can also significantly effect the predicted cetane numbers. If the CH_2/CH_3 ratio of sample 15 were 0.01 lower this would correspond to a decrease of 0.4 in the predicted cetane number. It has been found that the quality of NMR data varies from instrument to instrument⁵², therefore, it would be desirable for standards to be used to check NMR spectrometers in a similar way in which standards are used to check engines used in the engine test. Errors can also be present in the prediction formula since the cetane numbers of the fuels are not necessarily exact, having been tested on a single engine. It is also unlikely that a linear expression will be representative of the full cetane number range because the CH_2/CH_3 ratio tends to zero as the number of CH_3 groups increases. This was shown (Figure 3.9) by calculating the CH_2/CH_3 ratios of the n-alkanes from heptane to octadecane and two highly branched alkanes, heptamethylnonane, the low cetane number standard, and pentamethylheptane thus representing the two extremes of the cetane number scale. However, using a CH_2/CH_3 ratio alone, it is not possible to predict the cetane numbers of individual compounds such as an alkane with a single methyl branch because regardless of the placing of the methyl group, the CH_2/CH_3 ratio and therefore the cetane number will be the same.

In practice this is not the case, because 2-methylpentane and 3-methylpentane have cetane numbers of 33 and 30 respectively⁶⁰. To overcome this problem another parameter such as density would have to be determined and included in the data base. However, the difference between the two cetane numbers is relatively small and should not prejudice the results obtained with the derived methods.

The two prediction methods, PCN1 and PCN2, derived for synthetic fuels, were tested against the ¹H NMR methods of Gautier and Pande/Hardy which were derived for predicting the cetane numbers of crude-oil derived diesel fuels. For the samples tested the two PCN prediction methods are better predictors of cetane number. However, it is interesting to note from figure 3.10 that all the methods follow a similar pattern in that they all show an increase or decrease in cetane number at the same time. This indicates that the effect of alkane CH₂ and CH₃ groups on the cetane number of crude-oil derived or synthetic diesel fuels is similar for all the methods and the differences recorded must be caused by the different types of aromatics present in the fuels used in the data bases of Guatier and Pande/Hardy since the aromatic terms present in these methods are negative.

It was established that the cetane numbers of synthetic diesel fuels derived from other catalyst sources and feeds could be predicted with confidence using the derived correlations.

The catalytic oligomerization of short chain alkenes to a diesel product consisting of C10 and higher hydrocarbons depends on the operating parameters used in its production. Typical conversion versus temperature profiles obtained with ethene, propene and 1-butene feeds (Figure 3.2) show that with an increase in carbon chain length lower conversion levels are obtained. This can be partly attributed to steric effects and, in the case of 1-butene, partly attributed to mass transfer effects because at 35 bar and temperatures below 160°C 1-butene will be in the liquid phase. As the temperature is increased both the overall conversion and the %C10+ fraction increase. The production of this fraction is maximised in the 200 to 260°C temperature range. However, this type of data does not give an indication of the quality of the product as a diesel fuel.

It was also shown in the micro-reactor experiments that as the WHSV decreases the cetane number also decreases (Figure 3.11). With a decrease in WHSV it might be expected that the carbon number of the product would increase due to the increased residence time of the feed on the catalyst. For a diesel fuel derived from crude-oil an increase in carbon number generally results in an increase in cetane number (see Figure 1.5). However, the results show that for the synthetic diesel fuels this is not the case. The predicted cetane number of the hydrogenated 165°C - 180°C fraction of sample 3 (Table 3.1, cetane number = 39) was 48,8. This result suggests that the inclusion of this fraction could be expected to improve the cetane number of the fuel as a whole. It also shows that an increase in carbon number does not automatically mean that the cetane number of the product will also

increase. Other factors such as the degree of branching occurring in the product must also be taken into consideration.

A minimum pressure of 20 bar is required for the production of diesel range product from an ethene feed in the micro-reactor. However, between 20 bar and 50 bar, pressure does not appear to significantly affect the amount or the quality of the diesel range product. Similarly for the slurry reactor the predicted cetane number of the diesel range fuels remained constant even when using a WHSV of 12 g feed/g cat/h at 50 bar. One reason for this could be that although the WHSV of the feed is quite high, the residence time of the products in the reactor is long due to the large volume of the slurry reactor. This allows secondary reactions such as butene oligomerization to occur which increases the branching present in the product.

The effect of WHSV on the cetane number of the diesel range oligomerization product obtained from the micro-reactor was again reasonably constant being about 41 at space velocities of 2, 4 and 6g feed/g cat./h. At a space velocity of 1 the predicted cetane number was observed to drop sharply. The reason for this drop in cetane number with WHSV has already been discussed above.

Reaction temperature had a significant effect on the amount of diesel range product formed, rising from 12,5% by mass at 100°C to 49,8% at 255°C. At the same time however, the predicted cetane number of the diesel range product decreased from 40,2 to 27,3. A plot of the carbon number distribution of the product as a function of temperature showed

that as the temperature increased the conversion of the primary butene products increased in importance. Above 200°C more C8 than C6 hydrocarbons were being formed. It appears that at these temperatures two parallel oligomerization reactions are taking place. Ethene is converted to butene and higher molecular weight species and the butene formed is also converted to higher molecular weight species in a secondary reaction. If the large increase in diesel range product with increasing temperature is caused by these secondary butene oligomerization reactions this could explain the decrease in cetane number because engine test results of 1-butene oligomer diesel (section 3.1) had all been reported as being less than 35,2 when tested by SASOL.

The effect of temperature on the hydrogenated C₆ product obtained from ethene oligomerization was also quite significant. Since the oligomerization reaction follows a chain growth mechanism it was assumed that the products formed in the C₆ fraction would be typical precursors of the higher molecular weight products obtained in the C10+ (diesel) fraction. Theoretically, in the hydrogenated C₆ fraction the only products which should be formed are 3-methylpentane and n-hexane. It was shown that even at 55°C some structural isomerization occurs with the formation of small amounts of 2-methylpentane. Between 140°C and 210°C a significant change in selectivity occurred with a concurrent increase in the amount of branched products formed. Should there be a similar increase in the amount of branched products formed in the diesel range oligomerization product the result would again be a lower cetane number. These results provide supporting evidence for a co-ordination mechanism during oligomerization over the supported nickel catalyst at

temperatures up to 140°C. Acid catalysis may also be involved at temperatures greater than 140°C, accounting for the formation of 2,3-dimethylbutenes and 2-methylpentenes during ethene oligomerization and in the conversion of the primary butenes formed to higher molecular weight products. No conversion of ethene occurred when the catalyst was reduced with hydrogen. This showed that the nickel must be present on the silica/alumina support as Ni^{2+} or Ni^{1+} and not Ni^0 which is obtained by reduction in hydrogen.

On base pretreating the catalyst with ammonia to neutralise any possible acid sites on the catalyst surface the effect on ethene conversion was that the amount of C_{10+} formed remained approximately constant over the full temperature range tested. This suggests that acid sites were responsible for the large increase in the C_{10+} fraction with temperature previously observed with the untreated catalyst. An interesting observation is the decrease in conversion between 120°C and 170°C. This drop in conversion could be caused by the formation of high molecular weight products that remain on the catalyst surface. The predicted cetane number of the product obtained at 80°C was 43,3 which is a slight improvement over the untreated catalyst.

The results obtained with a diluted catalyst show that temperature fluctuations within the catalyst bed do not have a great effect on either the conversion or the cetane number of the diesel range product.

4.2 CONCLUSION

In conclusion this study shows that it is possible to predict the cetane numbers of hydrogenated diesel range oligomerization product from the average degree of branching as determined by ^1H NMR. The method is at least as accurate as the ASTM engine test. The technique is simple, fast, requires less than 1ml of sample, and has a direct application in the area of synthetic fuels research. The technique is limited, however, to accurately predicting the cetane number of alkane fuels only since other groupings were not present in the hydrogenated fuels analysed.

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